Mn/Ti layered double hydroxide: an investigation into the structure and electron transport through combinatorial experimental and theoretical approaches

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Abstract
Layered double hydroxides (LDHs) also known as hydrotalcite-like compounds that represent a broad class of lamellar basic inorganic compound possessing high capacity for anion intercalation. In this work, Mn/Ti LDH has been synthesized through a single step hydrothermal route using commercially available Mn(NO3)2.4H2O, TiCl4 and urea for investigation into the morphological and electron transport properties. The structural aspects and electron transport within the Mn/Ti LDH, has been investigated through a combinatorial approach of co-relating the experimental results with theoretical studies. The data mined crystal structure of the material, has been presented after comparison of the experimental XRD with the data mined XRD parameters. The characterizations suggest the material to possess crystallinity, layered structure, hexagonal morphology, good potentiodynamic electrochemical response, narrow multiple direct band gaps. The multiple narrow band gaps and electron transport properties could be evident through the UV-visible DRS and cyclic voltammetry analyses of the material. In order to theoretically establish electron transport, the experimental values of band gaps and ξ-potential results have been incorporated into the expression for the conduction-band energy (Ec) for generating the density patterns of the LDH through Monte Carlo simulations. Fermi–Dirac statistics presented the probability of transfer of electrons from VB to CB at different temperatures and for given energies for Mn/Ti LDH material. This work emphasized on the methodological advances associated with the structural and electron transport aspects of Mn/Ti LDH.

1. Introduction
Layered double hydroxides (LDHs) constitute a category of anionic clay materials which possess 2D layered matrices, represented by the general formula [MII1−xMIIIx(OH)2]x+(An−/n·yH2O. MII and MIII corresponds to the (+II) and (+III) cations and A− is the interlayer anion within the layered framework. The LDHs comprise of brucite-like layers, possess a fraction of M2+ cations (e.g. Mg2+, Fe2+, Co2+, Cu2+, Ni2+ or Zn2+ etc) octahedrally coordinated by –OH groups. The M2+ cations are substituted isomorphously by the M3+ cations (e.g. Cr3+, Ga3+, In3+, Mn2+, Ti3+ etc) that results positively charged layers. The interlayer anions compensate for the positive charge of the brucite layers. Moreover, H2O molecules associated with the interlayer galleries stabilize the layered structure by forming H–bonds to the H2O molecules as well as to the anions. The weak interlayer bonding along with its compositional variability of the LDHs results in its exceptional expandable properties and it finds extensive applicability as polymer fillers, catalyst supports, antacids, flame retardants.
trapping agents for anionic contaminants, polymer stabilizers, molecular sieves, ion-exchangers, adsorbents and novel materials with efficient photochemical properties [1–7]. LDHs also find extensive applicability in the field of medicine, thin films, conducting materials, electrodes and corrosion protection [8–12].

This work portrays the synthesis of Mn/Ti LDH through a single step hydrothermal route, whose formation mechanism has been illustrated from the standpoint of nucleation and self assembly induced through Ostwald ripening. The purpose of doping of Ti$^{4+}$ with Mn$^{2+}$ towards Mn/Ti LDH synthesis, is to extend the absorption of the LDH material to longer wavelength, that leads to higher photochemical performance. After photochemical excitation, Mn$^{2+}$ gets transformed to Mn$^{3+}$, which has tremendous electron trapping property that readily reverts back to Mn$^{2+}$. Moreover, the energy level for Mn$^{3+}$ is above the valence band edge of Ti$^{4+}$ ions therefore inducing photochemical efficiency [13–15]. The core crystal structure has been presented for the material after co-relation of the experimental XRD with the data mined XRD, generated using the Materials Project. Characterizations of the LDH nanomaterial reveals narrow band gap and good potentiodynamic electrochemical response that reflected the electron transport across the semiconductor material. Moreover, a simulation based practical realization of electron transport phenomenon within the LDH has been provided by Monte Carlo simulation. Fermi–Dirac statistics have also been employed to understand the pattern of changes in occupancy probability with changing energy and temperature for the LDH.

2. Characterization results

2.1. XRD analysis

The XRD pattern confirmed the material to be Mn/Ti LDH (figure 1). The characteristic reflection peaks (003), (006) and (009) are observed at 2θ values of 12.88°, 24.63° and 37.84° respectively, representing the hexagonal phase of the LDH [16–18]. The d-spacing (d$_{003}$) has been observed to be 0.688 nm (2θ = 12.88°), consistent with the literature reports representing the hexagonal phase LDH having interlayer CO$_3^{2-}$ and H$_2$O molecules. Hence, it is considered that Mn/Ti LDH nanomaterial, possessing similar basal spacing, is most likely to exhibit similarity in the planer orientation of the interlayer CO$_3^{2-}$ and H$_2$O molecules [19, 20]. Moreover, the peaks corresponding to (100), (015), (018), (1010), (113), (1013) and (116) could also be indexed to typical LDHs [21]. The addition of TiCl$_4$ within the aqueous reaction system during the Mn/Ti LDH synthesis has generated TiO$_2$ in its anatase and rutile phases; which could be evident by comparison of the XRD peaks of the LDH with the JCPDS data of the anatase and rutile phases of TiO$_2$. The peaks associated with the anatase (TiO$_2$) phase, in accordance with the JCPDS card no. 21–1272 could be indexed at the corresponding 2θ values- 28.03° {A (101)}, 47.80° {A (200)}, 53.98° {A (105)}, 55.18° {A (211)} and 60.51° {A (204)} within the LDH. Moreover, the peaks associated with the rutile (TiO$_2$) phase are observed at the corresponding 2θ values- 26.41° {R (110)} and 35.95° {R (101)} respectively in accordance with JCPDS card no. 21–1276. The existence of the rutile and anatase phase in the XRD pattern of the LDH also reflects the successful doping of Ti with Mn to form Mn/Ti LDH [22]. Moreover, the existence of narrow and sharp diffraction peaks indicates good crystallinity of the LDH material. The incorporation of TiO$_2$ is expected to induce higher charge transfer efficiency within the LDH. The x-ray crystallographic parameters are presented in S1 (supplementary information is available online at stacks.iop.org/MRX/6/125549/mmedia). Apart from the characteristic peaks, the small intensity peaks observed at 2θ values of 73.87° (d = 0.128 nm), 77.59° (d = 0.123 nm) and 78.40° (d = 0.122 nm) has also been found to very
closely match with the data mined XRD pattern, thereby confirming the validity of the data mined XRD pattern along with its generated core crystal structure.

The data mined XRD generated through Materials Project (an initiative of the Lawrence Berkeley National Laboratory, US that uses combination of web-based dissemination and open-source analysis with new dimensions for cracking the materials discovery problem) [23, 24] by considering Mn$^{2+}$, Ti$^{4+}$ and O$^{2−}$ as candidates for structure generation by high-throughput computation has been matched with the θ values and d-spacings of the experimentally observed XRD for Mn/Ti LDH material. The data mined XRD parameters are presented in S2 (table S2.1; supplementary information) and its associated data has been annexed in supplementary information 2. It is seen that the data mined XRD possess 80% matching with the experimentally observed XRD parameters for the Mn/Ti LDH in respect of 2θ values, d-spacing as well as lattice parameters. As a result of very high matching (80%) between the experimental and the data mined XRD, the core crystal structure, generated through data mining has been considered to be valid for Mn/Ti LDH material. Moreover, the data mined structure belonged to the hexagonal crystal system (figure 2(A)), which is also in accordance with the SEM and AFM results for the LDH. The experimental XRD and the calculated XRD parameters are found to be nearly same, and follows the hexagonal crystal system, in accordance with the SEM and AFM observations. Minor differences between the experimental and the calculated patterns could be attributed to the fact that the data mining has been performed considering Mn$^{2+}$, Ti$^{4+}$ and O$^{2−}$ as candidates for simulations excluding the –OH groups, CO$_3^{2−}$ species or other impurities that existed in reality within the actual LDH. The core crystal structure is presented in figures 2(A), (B) and the generated data is annexed in supplementary information 1. The hexagonal arrangement of atoms could be evident from figure 2(A) and the arrangement of atoms within the unit cell is presented in figure 2(B). The structure belonged to the hexagonal crystal system (in accordance with the SEM and AFM observations) having (α = β = 90°) and a = b = 0.5735 nm and c = 1.405 nm. The lattice parameter ‘a’ is found to be very close to that of its calculated value obtained using experimental XRD data (table S1; supplementary information). The minor difference in ‘c’ associated with the data mined structure and that calculated from the experimental XRD data could be attributed to the minor variation in the growth of the actual crystal along the c-axis.

2.2. SEM-EDAX analyses

The morphology of Mn/Ti LDH nanomaterial, investigated using SEM, exhibited porous morphology composed of hexagonal shaped house-of-cards-type stacking of hexagonal sheets (figure 3). The occurrence of hexagonal platelets, as seen in the SEM image, resulted from the subsequent crystallization of layered double hydroxide nanoparticles synthesized under hydrothermal conditions in basic medium [19–22, 25]. It is most likely, that the existence of CO$_3^{2−}$ species within the interlamellar space has produced a change in the superficial interaction between particles that has influenced the stacking of the particles in forming a 3D hexagonal architecture. The x-ray elemental maps of the LDH is presented in figure 4. The Mn/Ti weight ratio by elemental mapping was found to be (Mn : Ti :: 8 : 4) 2:1, exactly matching the stoichiometric ratio of Mn and Ti taken during the hydrothermal synthesis. Further, the EDX analysis showed the existence of C which corresponds to the interlayer CO$_3^{2−}$ species formed during the hydrothermal synthesis (as observed in the FT-IR analysis) within the LDH from the organic template urea that used as basic precipitant in the LDH synthesis. The
identification of O corresponds to –OH groups that stabilize the brucite sheets that carry \( \text{CO}_3^{2-} \) ions and \( \text{H}_2\text{O} \) in the interlayer positions. The identification of N and Cl is due to the use of urea (as basic precipitant) and TiCl\(_4\) during the LDH synthesis.

2.3. AFM analysis

Tapping mode (contact) AFM has been used extensively to investigate the morphology and thickness (along c-axis) of the Mn/Ti LDH material. The AFM also supported the SEM results revealing the existence of nearly hexagonal house-of-cards stacking of sheets (figure 5(A)) [16–18]. The hexagonal sheets have become slightly distorted owing to ultrasonication of the LDH sample prior to imaging. The surface topography revealed by the 3D AFM image showed a number of crests and troughs (figure 5(B)) within the (12 \( \mu \text{m} \times 12 \mu\text{m} \)) zone along with a stacked hexagonal Mn/Ti LDH crystallite; also observed in the SEM results. The existence of various crests and troughs in the AFM image might be due to the exfoliated and distorted crystal lattices, formed due to ultrasonication of the LDH sample. The overall 3D height profile revealed a maximum height of \( \sim 1.8 \mu\text{m} \) including all the crests and troughs seen within the selected (12 \( \mu\text{m} \times 12 \mu\text{m} \)) zone.

The height tracer (figure 5(C)) reveal the average height of the hexagonal crystallite to be \( \sim 0.924 \mu\text{m} \) (figure S3.1; supplementary information) which corresponds to almost 435 hexagonal unit cells possessing house-of-cards stacking one over the other (figure S3.2; supplementary information). Alternatively, this also indicates the growth of the lattice in Z (or c) direction, forming the microcrystal lattice.

2.4. FT-IR analysis

The FT-IR result of Mn/Ti LDH has been found to be consistent with the typical LDH materials having interlayer \( \text{CO}_3^{2-} \) anions and \( \text{H}_2\text{O} \) molecules (figure 6). The broad band at 3414 cm\(^{-1}\) corresponds to –OH stretching vibrations associated with the surface –OH groups and interlayer \( \text{H}_2\text{O} \) molecules. The shoulder at 3132 cm\(^{-1}\) could be attributed to the H–bonding among the surface –OH groups and interlayer \( \text{H}_2\text{O} \) molecules present within the LDH. Moreover, the bands at 1464 cm\(^{-1}\) (\( \nu_3 \)), 1385 cm\(^{-1}\) (\( \nu_2 \)), 1299 cm\(^{-1}\) (\( \nu_2 \)) could be due to the different bending vibrations associated with the \( \text{CO}_3^{2-} \) species present in the interlayers of the Mn/Ti LDH. The band at 1637 cm\(^{-1}\) could be attributed to the bending vibration of \( \text{H}_2\text{O} \) molecules. The bands arising at 1556 cm\(^{-1}\) and 1122 cm\(^{-1}\) could be attributed to the asymmetric and symmetric C–O\(_{\text{as}}\) vibrations of the interlayer \( \text{CO}_3^{2-} \) species respectively. The band at 1075 cm\(^{-1}\) could be attributed to C–O\(_{\text{as}}\) associated with \( \text{CO}_3^{2-} \) species. The band at 890 cm\(^{-1}\) is most likely due to in-plane quadrant bending of \( \text{CO}_3^{2-} \) species. The bands at 798 cm\(^{-1}\) and 615 cm\(^{-1}\) indicates the existence of metal–hydroxyl (M–OH) and metal–oxygen (M–O) groups present in the Mn/Ti LDH [16, 18–21].
2.5. Electrochemical characterization using cyclic voltammetry

Cyclic voltammetry has been performed to investigate the occurrence of electron transport across the LDH material. The electrochemical response of the Mn/Ti LDH nanomaterial was recorded using potential sweep cyclic voltammetry. Figure 7 at sweep rate of 0.1–0.5 mVs⁻¹. It is seen that at low potential regimes, the

![Figure 4](image_url)

**Figure 4.** (A) Selected area of Mn/Ti LDH sample chosen for EDX elemental mapping (B) Overall selected area X-ray map along with % composition. Regions of interest (ROI) in X-ray maps of (C) C K (D) N K (E) O K (F) Cl K (G) Ti K and (H) Fe K.
capacitive currents, resulting from the double-layer mechanism are negligibly small, compared to the peak currents at high potentials. Two redox couples are observed between 0.4 to 0.6 V and $-0.35$ to $-0.23$ V besides a steep increase in current beyond $-0.7$ V; corresponding to the existence of Mn and Ti within the LDH. The redox couples shifted with the increasing sweep rate between 0.1 to 0.5 mVs$^{-1}$. Moreover, it is seen that the peak-to-peak separation widened and the peak potential was observed to increase with the increasing sweep rate [22, 25]. The linearity in the increase of cathodic and anodic currents is indicative of the occurrence of a surface controlled electrochemical reaction. Moreover, the observed steep rise in the current with potential greater than $-0.7$ V corresponds to the occurrence of oxygen evolution reaction (OER) in accordance with the reaction-

$$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$$

Moreover, in the high potential regime, peak currents could be observed due to redox pairs occurring for anodic and cathodic sweeps respectively; the peaks in the voltammogram is most likely to correspond to oxidation and reduction of active materials according to the reaction-

$$\text{Mn(OH)}_2 + \text{HO}^- \leftrightarrow \text{MnOOH} + \text{H}_2\text{O} + \text{e}^-$$
It is seen that the peak current increase upon increasing the cycle number of the potential sweep. The potential difference between the anodic and cathodic peaks has been observed to increase with the number of cycles, which indicates that the resistance of electrolyte migration as well as that of electrical conduction has been magnified with cycling as a result of increasing thickness of the thin film formed on the electrode surface. As low scan rates are necessary for obtaining current-voltage curves, a scan rate of 0.5 mVs$^{-1}$ has been chosen to limit the overall time spent under OER conditions. It is seen that at slower scan rates, increasingly more bubbles are formed under OER conditions and are collected near the surface of the electrode. The accumulation of bubbles on the electrode surface resulted a drop in the measured current due to coverage of the active sites on the electrode surface. The enhancement of the $i_p$ values with increased scan rates signifies the sample to possess lower resistance and better reversibility. The potentiodynamic electrochemical response infers remarkable semiconductor properties to the LDH nanomaterial.

2.6. UV–vis DRS analysis

UV–vis DRS was employed for investigating the coordination state and nature of bonding of Mn and Ti within the LDH (figure 8). The LDH showed a strong absorption peak $\sim 246$ nm with an absorption edge starting from $\sim 336$ nm to $\sim 370$ nm that seemed to be followed by another band edge extending up to $\sim 450$ nm. A very small shoulder at $\sim 450$ nm that extends up to $\sim 650$ nm might correspond to the presence of Ti$^{n+}$ within the brucite

$$\text{Ti(OH)}_4 + \text{HO}^- \leftrightarrow \text{(OH)}_2\text{Ti(OOH)} + \text{H}_2\text{O} + \text{e}^- \quad (3)$$

$$\text{(OH)}_2\text{TiOOH} + \text{HO}^- \leftrightarrow \text{Ti(OOH)}_2 + \text{H}_2\text{O} + \text{e}^- \quad (4)$$

Figure 6. FT-IR spectra of Mn/Ti LDH.

Figure 7. Cyclic voltammograms of Mn/Ti LDH at different scan rates.
sheets or may also represent supramolecular guest-guest or guest-host interactions [16, 17]. The band gap of Mn/Ti LDH has been calculated using the Tauc equation [16] from the UV–vis DRS spectra:

\[ \alpha h\nu = K(h\nu - E_g)^n \]

where, \( \alpha \) represents the absorption coefficient, \( h\nu \) represents photon energy, \( K \) is the proportionality constant, \( E_g \) represents the optical band gap energy and \( n \) represents the nature of the transition. When \( n = \frac{1}{2}, \frac{3}{2}, 2 \) or 3, the transition is direct allowed, direct forbidden, indirect allowed or indirect forbidden respectively.

Here, taking \( n = \frac{1}{2} \), the UV–vis DRS absorption data was fitted to allowed direct transitions across the energy band gap to obtain \( (\alpha h\nu)^{1/2} \) versus \( h\nu \) (eV) plot. The extrapolated value (to X-axis) of \( h\nu \) at \( \alpha = 0 \) presented three band gap values respectively- \( E_g = 1.14 \) eV, \( E_g' = 3.23 \) eV and \( E_g'' = 3.61 \) eV for the LDH (figure 9). The band gap, \( E_g = 1.14 \) eV is most likely due to Mn\(^{2+} \) 3d(t\(_{2g}\)) \( \rightarrow \) Mn\(^{2+} \) 3d(e\(_g\)) transition [18], whereas \( E_g' = 3.23 \) eV might be aroused due to ligand-to-metal-charge transfer (LMCT) of O 2p \( \rightarrow \) Mn\(^{2+} \) 3d (e\(_g\)) [18, 19]. The band gap \( E_g'' = 3.61 \) eV could be attributed to the existence of CO\(_3^{2−}\) groups in the LDH interlayer.

3. Interpretation of electron transport by Monte Carlo simulation

Photochemical reaction occurs due to the excitation of semiconductor materials by photons. In this work, a theoretical interpretation of the electron movement across the band gap of the Mn/Ti LDH has been established, that has resulted in exhibiting a remarkable electron transport property due to which a higher...
photochemical efficiency is observed. The electronic movement throughout the semiconductor LDH was correlated by using the result of characterizations in running the Monte Carlo simulations, which produces a dependent sequence (a chain) of random variables having approximate distribution. The simulation using Monte Carlo technique follows a two tier process; the firstly a sequence of values where simulated from the suggested distribution; and in the second part that simulated values are used to provide an empirical summary of the characteristics using the simulated values that share the same distributional properties. The co-relation is done by incorporating the value of conduction band energy ($E_c$) of the LDH [which in turn, is calculated using the value of direct band gap ($E_g$) of the Mn/Ti LDH (calculated using Tauc plot; obtained through UV-visible DRS)] to the energy density equation for determination of theoretical energy density, $g(E)$, using multi-electron Monte Carlo simulation. LDHs are known to possess n-type semiconductor properties [16–18], therefore in order to investigate the semiconductor properties of the LDH theoretically, the dynamics of electron transport is studied under Monte Carlo simulation conditions, assuming that the traps existing on the surface or grain-boundaries of the LDH are exponentially distributed on the energy scale in space. The approximation of pattern and behavior of energy density, $g(E)$; where the defects are assumed to be exponentially distributed on the energy scale within the LDH is considered to be of the form as discussed by Liu and Zhao (2014) [5], Ansari-Rad et al. (2012) [26], and Ansari-Rad et al. (2014) [27].

$$g(E) = \frac{N_t}{k_B T_0} e^{\frac{E - E_0}{k_B T_0}}$$

where, $N_t$ (1.0 × 10$^6$) denotes the number of traps, assumed to be uniformly distributed in a 100 × 100 × 100 cubic box, with periodic boundary condition being considered, $k_B$ (=1.38 × 10$^{-23}$ JK$^{-1}$) represents Boltzmann constant, $T_0$ is the trap depth (in Kelvin) and $E_0$ represents the conduction band energy of the semiconducting LDH [28]. The pattern of density for the LDH has been approximated under two different conditions. Firstly, in respect of transference of electron from VB to CB, a situation is considered where, there exist a sufficiently large energy gap and, the probability of transference of electron from VB to CB is very small and in order to investigate this extreme situation, it has been assumed that $E_c = 0$, i.e. unknown. Secondly, the pattern of the density is approximated for value of $E_c$ obtained empirically, by using the experimentally observed value of direct band gap ($E_g$); calculated using the UV-Visible DRS, in accordance with the following equation-

$$E_c = -\chi_{\text{oxide}} + 0.5 E_g + 0.059 (\text{PZZP} - \text{pH})$$

Hence, the value of valence band energy ($E_v$) follows the following equation:

$$E_v = -\chi_{\text{oxide}} - 0.5 E_g + 0.059 (\text{PZZP} - \text{pH})$$

where, $\chi$ is absolute electronegativity for each metal oxide phase associated with the LDH; $E_g$ is band gap of the LDH and PZZP is point of zero zeta-potential of the corresponding mixed metal oxide [16, 29–31]. The PZZP (=6.9) value was determined by using zeta-potential technique over a pH range of 3–12 (S4; supplementary information). The value of $E_v$ is calculated at pH = 6.9. The absolute electronegativity was calculated by using the set of following set of equations [16–]

$$\chi (\text{eV}; \text{A}_x \text{B}_y \text{O}_z) = (\chi_A^x \chi_B^y \chi_O^z)^{\frac{1}{x+y+z}}$$

where, $\chi$ (eV; elements) is the electronegativity of elements in eV scale; $E_{1b}$ and $E_{1a}$ are, respectively, the first ionization energy and first electron affinity of the elements in eV scale; and $\chi_{\text{oxide}} (\text{eV})$ represents the absolute electronegativity of the oxide in eV scale. The approximated formula of the mixed metal oxide is calculated using SEM/EDX data and is found to be Mn$_{0.67}$Ti$_{0.33}$O$_{1.33}$ (S8; supplementary information), and for this mixed oxide, $\chi_{\text{oxide}} (\text{eV})$ is calculated as 5.53 eV (S6; supplementary information). The $E_g$ value was calculated using equation (7) and the three $E_g$ values were recorded as −4.96 eV ($E_{g}$), −3.92 eV ($E'_{g}$) and −3.73 eV ($E''_{g}$) corresponding to the observed three band gap values $E_{g} = 1.14$ eV, $E'_{g} = 2.32$ eV and $E''_{g} = 3.61$ eV respectively for the LDH. The respective $E_v$ values were calculated using equation (8) as $-6.10$ eV ($E_v$), $-7.15$ eV ($E_v$) and $-7.34$ eV ($E_v$).

In order to approximate the pattern of energy density under both these situations Monte Carlo technique has been adopted, which produces a dependent sequence (a chain) of random variables having approximate distribution [29–33]. In accordance with the works of Ansari-Rad et al. (2012) [26] and Liu and Zhao (2014) [5], wherein the pattern of exponential energy density of states were presented for different $T_0$, ranging between 600–800 K and 800–1200 K, respectively; in this work for understanding the distributional pattern of $g(E)$, due to $T_0$ and the conduction band energy ($E_c$) of the LDH, the density pattern has been evaluated at two different $T_0$ viz., 800 K and 10 000 K under the sets of conditions where $E_c = 0$, −3.73, −3.92 and −4.96 eV and are illustrated in figures 10(A), (B).
Monte Carlo simulation revealed that for a particular temperature, the density follows the same distribution pattern, irrespective of conduction band energy ($E_c$) values. Figures 10(A), (B) presented the region wise distribution of the number of molecules in the energy density curve at different temperatures, under the boundary conditions ($E_c = 0, -3.73, -3.92, -4.96$ eV) more explicitly. It is seen that at $T_o = 800$ K, some of the electrons are found to possess either very low or very high energy density; and mostly the electrons are found to occupy the region of the curve around the high peaks and is located around the average energy of the electrons. On increasing trap depths, $T_o$ at 10 000 K, it is observed that average energy distribution curves showed an identical electron distributional pattern. Alternatively, it can also be interpreted that density follows a definite pattern at each $T_o$, independent of the conduction band energy ($E_c$) of the semiconductor LDH [31–39].

The broader context behind the independent conduction band energy of a semiconductor material; associated with the energy density distribution, could be explained on the basis of the fact that at very high $T_o$ (10 000 K), the particles/molecules lose their individual property, and is most likely to get transformed to the plasma state or high energy state at such a high trap depths, where the constituent atoms behave independently in a definite manner, irrespective of the nature of the inherent semiconductor LDH.

In order to have a deep understanding into the variation of energy density distribution with temperature, 3D-density distribution patterns of the LDH, were compared with the density at $T_o = 10 000$ K for both $E_c = 0$ and $E_c = -3.73, -3.92, -4.96$ eV (figures 11(A)–(D)). The variation of the overall shape of the density distribution curve with increasing trap depths from 800 K to 10 000 K, is evident under both the boundary conditions ($E_c = 0$ eV and $E_c = -3.73, -3.92, -4.96$ eV). The overall shapes of the energy density curves are observed to vary with changes in $T_o$. However, each of the density curves has been found to follow the similar distribution pattern, towards the axis, associated with the 10 000 K, which is due to the fact that at higher energy state, the constituent atoms behave independently in a definite manner, irrespective of the nature of the inherent material [40–43].

The distributional pattern of the traps, that has been assumed to be exponentially distributed on the energy scale within Mn/Ti LDH can be formulated as-

![Figure 10. Density distribution curve w.r.t energy for Mn/Ti LDH, compared at different values of $E_c = \{0, -3.73, -3.92$ and $-4.96\}$ eV at trap depths (A) 800 K and (B) 10 000 K.](image-url)
Under the circumstances when the energy gap between VB to CB is considered to be sufficiently large, wherein it has been assumed that $E_C = 0$ (unknown) then,
which implies that

\[ g(E, E_c = 0) = \frac{N_e}{k_B T_0} e^{\frac{E}{k_B T_0}} \]

(12)

which implies that

\[ g(E, E_c) = e^{\frac{E}{k_B T_0}} g(E, E_c = 0) = C(E_c, T_0) \, g(E, E_c = 0) \]

(13)

i.e. \( g(E, E_c) \) is \( C(E_c, T_0) = e^{\frac{E_c}{k_B T_0}} \) times the \( g(E, E_c = 0) \).
From equation (13) we have,

$$\frac{g(E, E_c)}{g(E, E_c = 0)} = C(E_c, T_0) = e^{\frac{E}{k_B T_0}} \quad (14)$$

Let $E_c < 0$ then as $T_0 = 0$, $C(E_c, T_0) \to 0$ and as $T_0 \to \infty$, $C(E_c, T_0) \to 1$. This suggest that at $T_0 = 0$ K, the ratio $\frac{g(E, E_c)}{g(E, E_c = 0)}$ would converge towards zero whereas at very high $T_0$ the ratio would converge to 1, i.e.,

$g(E, E_c) \to g(E, E_c = 0)$.

In order to draw an insight into the probability of an energy state occupied by electrons within the lattice of Mn/Ti LDH, Fermi–Dirac statistics is employed, which is based on the following equation-

$$f(E) = \left(1 + e^{\frac{E}{k_B T}}\right)^{-1} \quad (15)$$

where, $f(E)$ denotes the probability of occupancy of an electron in energy state $E$, $k_B$ is the Boltzmann constant and $T$ is the temperature in Kelvin scale. Figure 12(A) represents three dimensional pattern showing changes in occupancy probability based on Fermi–Dirac statistics with changing energy and temperatures, and figure 12(B) presents the contour plot of the occupancy probability. The changes in both occupancy probability and contour plot reveal that at zero Kelvin temperature, the occupancy probability of an electron is certain i.e. $f(E) = 1$, represented in the red highlighted region of both the plots. This indicated a higher probability of occupancy of
lower energy state, by an electron, than a higher energy state. However, with increase in temperature, it is seen that the probability, \( f(E) \) increases; such that a higher occupancy probability has observed for a high energy state, at higher temperature, than that observed at lower temperatures. Moreover, it is also seen that at extremely high temperature (\( T \rightarrow \infty \)) the occupancy probability takes a fixed value and converges to probability of 0.5 i.e. \( f(E) \rightarrow \frac{1}{2} = 0.5 \). Thus Fermi–Dirac distribution function visualized the behavioral changes associated with the probability of an energy state occupied by electrons with changing temperatures.

4. Conclusions

Thus Mn/Ti LDH exhibited hexagonal morphology with multiple narrow band gaps, indicative of the occurrence of various types of electronic transitions within the material. The crystal structure generated after validation of the experimental XRD with that of the data mined XRD belonged to the hexagonal crystal system, in good agreement with the SEM and AFM observations of the LDH material. The phenomenon of electron transport interpreted experimentally through UV-visible DRS and cyclic voltammetry has also been combinatorially explored through Monte Carlo simulations by incorporating the experimentally observed values of band gaps and \( \xi \)-potential results into the mathematical expression for the conduction-band energy (\( E_c \)) of the material. The Monte Carlo simulations reveal that although the overall shapes of the energy density curves varies with changing trap depths, each of them has been found to follow the similar distribution pattern; revealing the broader aspect that at very high energy state, the constituent atoms behave independently in a definite manner, irrespective of the nature of the inherent semiconductor material. Moreover, the probability of electron transfer from the VB to CB has been successfully estimated through Fermi–Dirac statistics with changing temperatures for the LDH. This work thus provided an advancement into the structural aspects and electron transport properties of Mn/Ti LDH undertaken combinatorially through experimental and theoretical studies.

5. Experimental section

5.1. Materials

The A.G. chemicals- Mn(NO₃)₂.4H₂O, TiCl₄, urea, KOH were procured from Merck Chemicals, USA and used without further purification. Deionized water (conductivity \(< 0.15 \text{ mS cm}^{-1}\)) was used throughout the experiments. The chemical information of the reagents used in this work are presented in table 1.

5.2. Hydrothermal synthesis of Mn/Ti LDH

The typical synthesis of Mn/Ti LDH involved the dissolution of 10.97 g of Mn(NO₃)₂.4H₂O, 1.1 ml TiCl₄ along with 3.0 g of urea in 100 ml of deionised water, followed by vigorous stirring of the reaction mixture for 2 h at room temperature. The mixture has been subjected to hydrothermal treatment on a Teflon lined autoclave at 140 \( ^\circ \text{C} \) for 48 h. The light brown crystalline product (extracted after centrifugation) was washed with water, dried at 100 \( ^\circ \text{C} \) for 4 h. The steps of hydrothermal synthesis of Mn/Ti LDH is schematically illustrated in figure 13.

5.3. Characterization techniques

The X-ray diffraction pattern for the LDH has been recorded on a PANalytical X’Pert PRO diffractometer. The Reflection mode analyses have been set up using the conventional Bragg–Brentano geometry. The incident Cu Kα, x-ray beam (40 kV, 30 mA) has been passed through a 0.02 rad Soller slit, a 1/8 divergence slit, a 15 mm fixed mask, and 1/4 anti-scatter slit. A PIXcel linear sensitive detector fitted with a \( \beta \) filter, a 0.02 rad Soller slit, and a 1/8 anti-scatter slit was used to detect the diffracted beam. The X-ray diffraction patterns were recorded between 5° and 80° (2θ) with a step size of 0.02° and an acquisition time of 0.4 s per step. The transmission mode analyses has been recorded with the help of an elliptic focusing mirror, a 0.5° divergence slit, a 0.5° anti-scatter slit and a 0.02 rad Soller slit within the primary beam. The morphology and elemental composition of Mn/Ti LDH was investigated using a Zeiss Gemini SEM (5 kV)/EDX under an accelerating voltage of 15 kV. Gold coating of the LDH specimen has been performed ~6 nm/min (at pressure of \( 7 \times 10^{-2} \) Pa and current 20 mA) with Quorum(Q 150 R ES).

The layered framework and the lattice fringe separation within the LDH has been investigated using a JEOL JEM-2010 HR-TEM at an accelerating voltage of 200.0 kV. The surface topography of the LDH was measured by atomic force microscopy (Oxford instruments; Cypher Asylum Research, equipped with ARC2 controller) using a Si tip of 10 nm radius. The LDH sample was dispersed in EtOH by ultrasonication for ~5 min, followed by spreading the dispersion over a glass slide and
Table 1. Details of the chemicals as purchased from Merck chemicals, USA (M.P.- melting point; B.P.- boiling point).

| Chemicals                  | Formula          | CAS Reg. No | Molar mass/(g/mol) | Mass fraction | M.P./°C | B.P./°C | Density/(g cm⁻³ (20 °C) | Solubility/(g l⁻¹) |
|----------------------------|------------------|-------------|--------------------|---------------|---------|---------|------------------------|-------------------|
| Manganese(II) nitrate tetrahydrate | Mn(NO₃)₂·4H₂O     | 20694–39–7  | 251.01             | ≧98.5%        | 37      | —       | 2.13                   | 3800              |
| Titanium (IV) chloride      | TiCl₄            | 7550–45–0   | 189.68             | ≧97.0%        | —       | 136     | 1.728                  | —                 |
| Urea                       | CO(NH₂)₂         | 57–13–6     | 60.06              | ≧99.0%        | 133     | —       | 1.34                   | 1000              |
| Potassium hydroxide         | KOH              | 1310–58–3   | 56.11              | ≧85.0%        | 360     | —       | 2.04                   | 1130              |
subsequently dried. The ultrasonication has been done in order to open up the aggregated particles to single nano layer or at least a few stacked nanolayers. Height-mode images were recorded simultaneously with $512 \times 512$ pixel and 1–2 Hz scan rate.

Fourier transform infrared spectrum (FT-IR) was investigated using a Shimadzu FT-IR 3000 spectrometer within a wavelength range of 400–4000 cm$^{-1}$. The LDH sample was mixed with KBr in weight ratio 1:100 and compressed to form pellets for analysis.

The electrochemical characterization of Mn/Ti LDH based on cyclic voltammetry was performed using an electrochemical workstation (CHI 760 E, CH Instrument, Shanghai, China) to investigate the occurrence of electron transport. The cyclic voltammetry experiments were performed using a conventional three-electrode system; the working electrode being a modified glassy carbon electrode (GCE), Ag/AgCl (sat. KCl) electrode acted as the reference electrode and Pt wire acted as the counter electrode. KOH (1 M) solution is used as the electrolyte.

The UV-visible diffuse reflectance spectroscopy of the LDH was recorded using a Hitachi U4100 spectrometer, equipped with integrating sphere attachment having BaSO$_4$ background.

The dynamic light scattering experiments of the LDH at different pH levels has been analysed using a Malvern Zetasizer Nano ZS instrument.

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Notes

The simulations were carried using R-software version-3.4.1.

Conflicts of interest

There are no conflicts of interest to declare.

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