Empirical Modeling of Electron Transport in Fe/Ti Layered Double Hydroxide Using Exponential, Gaussian and Mixed Gauss–Exponential Distribution

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ABSTRACT: Fe/Ti-layered double hydroxide (LDH) has been hydrothermally prepared and characterized using X-ray diffraction, scanning electron microscopy, atomic force microscopy, Fourier transform infrared spectroscopy, and UV–visible diffuse reflectance spectroscopy for evaluation of its structure, morphology, and optical properties. The purpose of doping Ti4+ with Fe3+ toward the synthesis of Fe/Ti LDH is to extend the absorption of the nanomaterial to longer wavelength, which is known to exhibit higher electron transport performance. To provide a practical realization, electron transport modeling across the band gap has been interpreted using exponential, Gaussian, and mixed Gauss–exponential distribution. The conduction band energy ($E_C$) has been calculated by using the observed values of band gap ($E_g$) and $\xi$-potential of the LDH. A detailed study has been undertaken to investigate the pattern of theoretical density of the LDH on the basis of unknown ($E_C = 0$) and known (calculated) values of $E_C$. Fermi–Dirac statistics has been used extensively for estimating the occupancy probability of electron (e−)–hole (h+) pair formation within the valence and conduction bands, respectively, with different temperatures, as well as for given energy levels. Monte Carlo simulations have also been performed to evaluate the suitability of the choice of the model, on the basis of the probability of availability of e− within the conduction band. To provide a practical realization of the suggested models, electronic transition across the band gap of Fe/Ti LDH has been extensively investigated.

1. INTRODUCTION

The electron transport phenomenon occurs with the excitation of semiconductors by photons.1,2 The semiconducting properties of layered nanomaterials by light having energy sizeable to the band gap energy of the nanomaterial promotes e−s to the conduction band (CB), thereby generating h+ s within the VB

$$\text{semiconductor} \rightarrow e_{CB}^- + h_{VB}^+ \quad (1)$$

These generated e−–h+ pairs may recombine, releasing energy in the form of heat resulting no chemical changes within the nanomaterial. Without recombination, if the e−s and h+ s move to the surface, then the nanomaterial is expected to attain semiconducting property and can participate in a variety of redox reactions with adsorbed organic/inorganic molecular or ionic species. The redox reactions taking place over the surface of the semiconducting nanomaterials form the basis of photochemical reactions. The mechanism of e−–h+ hopping conduction model for basic semiconduction process is presented in Figure 1A. The usefulness of the semiconduction mechanism could be demonstrated with the help of $h_{VB}$ within the catalyst surface that induces oxidative decomposition of the material. The semiconductor materials also exhibit catalytic activities due to effective e−–h+ pair separation. The phenomenon of photosensitization in a basic semiconductor nanomaterial is shown in Figure 1B.

Layered double hydroxides (LDHs) possess inorganic layered matrices, generally represented as $[\text{M}_1\text{M}_2(\text{OH})_2]\text{A}^{n-}(\text{H}_2\text{O})_y$, where MII and MIII represent di- and trivalent metal cations, respectively, and A− is a charge-balancing anion. LDHs comprise brucite-like layers, having MII ions (e.g., Mg2+, Fe2+, Co2+, Cu2+, Ni2+, or Zn2+) octahedrally coordinated by −OH groups and a fraction (x) of MIII ions (e.g., Al3+, Cr3+, Ga3+, In3+, Mn3+, Ti3+, or Fe3+) that isomorphously substitute MII ions in brucite-like layers and, hence, result in positively charged layers.

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positively charged brucite layers are counterbalanced by the interlayer anions ($A^{n−}$). H$_2$O molecules exist within the interlayer galleries. The −OH groups are directed toward the interlayer spacing and may have been engaged in H-bonding with H$_2$O molecules as well as with the anions. The relatively weak H-bonding between the brucite layers enable LDHs to exhibit an expanding nature. LDHs are also considered as doped semiconductors having compositional variability, and hence they find extensive applicability as novel materials with efficient photochemical functions.\textsuperscript{3−5} The semiconduction mechanism exhibited by LDHs occurs as a result of the transfer of e$^-$s from the valence band (VB) to the conduction band (CB). The purpose of doping Ti$^{4+}$ with Fe$^{3+}$ toward the synthesis of Fe/Ti LDH is to create band states, thereby favoring electronic transition and resulting in narrowing the band gap, which is known to exhibit higher photochemical performance. Moreover, Fe$^{3+}$ also acts as a photogenerated electron trapper, since the energy level for Fe$^{3+}$ ions is above the valence band edge of Ti$^{4+}$ ions, therefore inducing higher electron transport efficiency. Fe$^{3+}$ also possesses a stable half-filled (3$d^{5}$) electronic configuration, and the trapped charge could easily transform Fe$^{3+}$ to Fe$^{2+}$ and could also migrate to the surface for participation in various photochemical reactions. The present work portrays the synthesis of Fe/Ti LDH by a single-step hydrothermal route and its characterization results by adopting the Monte Carlo simulation procedure. The electronic transition across the band gap of the LDH has been demonstrated for realization of the suggested models.

2. CHARACTERIZATION RESULTS

2.1. X-ray Diffraction (XRD) Analysis. XRD patterns confirmed the material to be Fe/Ti LDH (Figure 2). The strong reflection peaks at (003), (006), (009), (110), (113), (100), (011), (018), and (1013) represent the characteristic hexagonal phase of LDHs.\textsuperscript{2−8} The $d$-spacing ($d_{003}$) was 0.70 nm ($2θ = 12.69°$), consistent with the previous reports of hexagonal phase LDHs with interlayer CO$_3^{2−}$ and H$_2$O molecules. Since Fe/Ti LDH exhibited similar layer thickness to normal LDHs, it is most likely that planar orientation of anions has been exhibited mainly by CO$_3^{2−}$ and H$_2$O molecules, in the interlayer gallery of Fe/Ti LDH (Figure S1.1; Supporting Information).\textsuperscript{3,6} The incorporation of TiCl$_4$ during the aqueous phase LDH synthesis has generated TiO$_2$ in its anatase phase, which is evident from the (110) and (101) diffraction peaks present at $2θ$ values of 27.99 and 33.20°, respectively, in the X-ray diffractogram of Fe/Ti LDH. The existence of the characteristic peaks of Ti (anatase) phase within the X-ray diffractogram further indicates the successful doping of Ti within the synthesized LDH material. Moreover, TiO$_2$, in anatase form, exhibits high charge transfer efficiency and introduces defect states within the LDH.\textsuperscript{7,8} It also helps in narrowing the band gap. The narrow and sharp diffraction peaks indicate the existence of well-defined crystalline phases in Fe/Ti LDH. The X-ray crystallographic parameters are discussed in S1 (Supporting Information).

2.2. Scanning Electron Microscopy (SEM)—Energy-Dispersive X-ray (EDX) Analysis. SEM and EDX mapping of the LDH sample have been performed to have an insight into the morphology of the LDH nanomaterial. The SEM image (Figure 3) confirmed the presence of ultrafine regular hexagonal-shaped nanolayers stacked one over the other representing the lamellar phase of LDH materials.\textsuperscript{3,10} The regular hexagonal particles existed due to the subsequent crystallization of LDH incorporated with simple interlayer anions and H$_2$O molecules owing to hydrothermal treatment. The existence of distorted hexagonal particles is most likely due to the ultrasonic treatment of the sample prior to SEM imaging. The X-ray elemental maps of the Fe/Ti LDH sample are presented in Figure 4. The Fe/Ti weight ratio by elemental mapping was found to be 2.125:1, nearly equivalent to the stoichiometric ratio of 2:1 Fe/Ti LDH (corresponding to the weight ratio Fe/Ti = 2.33:1) of Fe and Ti taken during the hydrothermal synthesis.

Figure 1. Schematic diagram of a semiconductor nanomaterial exhibiting (A) e$^−$→h$^+$ hopping conduction and (B) photosensitization.

Figure 2. XRD spectrum of Fe/Ti LDH.
observed at lower wavenumber in the LDH rather than assigned for free H₂O at 3600 cm⁻¹. The shoulders at 2973 and 2848 cm⁻¹ might be due to the H-bonding among the surface –OH groups, interlayer H₂O, and CO₃²⁻ anions present in the LDH system. The sharp peak at 1800 cm⁻¹ appearing in the spectra could be due to the C=O vibrations, which correspond to the existence of interlayer CO₃²⁻ species. The absorption band at 1635 cm⁻¹ could be attributed to the H–O–H bending vibrations. The bands at 1549 and 1125 cm⁻¹ might be due to the asymmetric and symmetric vibrations, respectively, i.e., C–O₃vibrations of CO₃²⁻ species present in the system. Moreover, the bands at 1418 cm⁻¹ (v₂), 1187 cm⁻¹ (v₁), and 1122 cm⁻¹ (v₂) might also be due to the bending vibrational modes of interlayer CO₃²⁻ species and the band at 865 cm⁻¹ might be due to the in-plane quadrant bending vibration mode of CO₃²⁻. The bands at 720 and 614 cm⁻¹ confirm the presence of metal–hydroxyl (M–OH) and metal–oxygen (M–O) groups associated with the Fe/Ti LDH. The existence of these IR bands indicates the successful preparation of Fe/Ti LDH and the presence of CO₃²⁻ and H₂O molecules in its interlayer galleries.

### 2.5. UV–Visible Diffuse Reflectance Spectroscopy (UV–vis DRS) Analysis

UV–vis DRS was employed for investigating the coordination state and nature of bonding of Fe and Ti within the LDH (Figure 7). The strong absorption peak at ∼320 nm extending up to 450 nm could be indexed to Fe(II) coordinated to CO₃²⁻ within the interlayer galleries. A shoulder starting at ∼455 nm and extending up to 650 nm is most likely due to the presence of Ti⁺⁺ within the brucite sheets or may be a result of supramolecular guest–guest or guest–host interactions. The band gap of the LDH has been calculated using the Tauc equation from the UV–visible diffuse reflectance spectra

\[
\alpha hν = K(\nu - E_g)^n
\]

where \(E_g\) represents the optical band gap, \(hν\) represents photon energy, \(K\) is a constant, and \(n\) depends on the nature of the transition. In fact, \(n\) assumes values of 1/2, 2, and 3 for direct allowed, direct forbidden, indirect allowed, and indirect forbidden transitions respectively. In this case, the best fit of \((\alpha hν)^{1/2}\) versus \(E\) (eV) was obtained for \(n = \frac{1}{2}\), suggesting allowed direct transitions across the energy band gap. The extrapolated value (the straight line to the X-axis) of \(hν\) at \(α = 0\) gives a band gap value of 2.65 eV for the LDH (Figure 7 inset plot). The narrow band gap exhibits the LDH to possess remarkable semiconducting property. Moreover, the band gap is most likely due to the direct electronic transition from oxygen 2p to the metal ns or np levels. This also suggests that c’=h’ pairs could be photogenerated within the LDH by irradiation with light of longer wavelength. The narrow band gap of the LDH might also be due to the gap states induced by Ti⁺⁺ species, associated with oxygen vacancies within the layered structure.

### 3. ELECTRON TRANSPORT MODELING ACROSS THE BAND GAP OF Fe/Ti LDH

An investigation into the electron transport across the band gap of the Fe/Ti LDH was done using the multielectron Monte Carlo simulation procedure by incorporating the value of conduction band energy \(E_c\) of Fe/Ti LDH (which, in

![Figure 3. SEM image of Fe/Ti LDH.](image-url)
turn, is calculated using the value of direct band gap \( (E_g) \) (calculated using Tauc plot; obtained through UV–visible DRS analysis)) to the energy density equation for determination of theoretical energy density.

To understand the theoretical concept of electron transport across the semiconductor LDH, it is assumed that the defects/traps are uniformly distributed in a cubic \((100 \times 100 \times 100)\) box with periodic boundary condition.\(^\text{16–22}\) The exponential distribution has been employed for interpretation of electron transport across Fe/Ti LDH. Moreover, the electronic movement across the LDH has also been interpreted by applying Gaussian and mixed Gauss–exponential distribution for the first time in this work. A comparative study of the theoretical models has also been presented herein. The Monte Carlo procedure has been adopted for providing the simulation-based realization of electron transport. Therefore, a system is considered to possess \( N \) number of electrons, where \( N_c \) and \( N_v \) denote the number of electrons in the CB and VB, respectively, so that the total number of electrons is represented by

\[
N = N_c + N_v
\]
At a given temperature $T$ (K), the shifting of electrons from VB to CB depends upon the incident energy on the LDH. The energy (eV) incorporated to the system is denoted by $E = \varepsilon$ at the prefixed temperature $T$. Let $N_c(\varepsilon, t) = N(\varepsilon)$ represent the number of electrons shifted from VB to CB. Consequently, the number of electrons remaining in the VB at the same temperature would be $N_v(\varepsilon) = N - N_c(\varepsilon)$ (from eq 3). The availability of $N_c(\varepsilon)$ electrons in the CB at a given temperature and energy $\varepsilon$ is assumed to follow a binomial distribution $(N, p_\varepsilon)$, which is represented as

$$P(N_c(\varepsilon) = n_\varepsilon) = \binom{N}{n_\varepsilon} p_\varepsilon^{n_\varepsilon} q_\varepsilon^{N-n_\varepsilon}; n_\varepsilon = 0, \ldots, N; p_\varepsilon, q_\varepsilon \in [0, 1]$$

where $p_\varepsilon$ denotes the probability that at energy level $\varepsilon$ in the CB would be populated by at least one electron. Hence, the component $(1 - p_\varepsilon) = q_\varepsilon$ denotes the probability of nonmovement electrons to CB from VB (which is equivalent to the condition when no h$^+$ ions are formed in the VB). Hence, at the given energy level, the mean number of e$^-$s, $E(N_c(\varepsilon))$, transferred to CB at constant temperature and its variance, $V(N_c(\varepsilon))$, which was obtained using eq 4, have been presented herein as

$$E(N_c(\varepsilon)) = NP_\varepsilon$$

$$V(N_c(\varepsilon)) = NP_\varepsilon(1 - p_\varepsilon)$$

Moreover, the occupancy of e$^-$ at CB has been determined by the probability of transfer of at least one e$^-$ from the VB to CB, at the energy level $E = \varepsilon$ for the given fixed temperature $T$. The energy $E = \varepsilon$ delivered to the system is supposed to be divided

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**Figure 5.** (A) Three-dimensional (3D) AFM surface topography, (B) two-dimensional (2D) AFM surface topography, and (C) height profile of Fe/Ti LDH.

**Figure 6.** FT-IR spectrum of Fe/Ti LDH.

**Figure 7.** UV–visible diffuse reflectance spectrum and Tauc plot (inset plot) of Fe/Ti LDH.
into “m” nonoverlapping equal subintervals, where m is considered to be a positive integer, then each corresponding subinterval $\Delta E = e^*/m$ could be assumed to be an infinitesimally small energy level. The probability of transfer of an $e^-$ to CB from VB in the energy interval $\Delta E$ would therefore be $\binom{m}{g}e^*/m$ and the probability of nontransfer would be $(1 - m/e^*)^g$. The electron jump has been considered only when at least one $e^-$ shifts from VB to CB in the $j$th energy gap such that $j \geq 1, \ldots, m$. According to the law of total probability, the distribution of number of $e^-$ in the CB could be represented as

$$P_C = \sum_{g=k}^{m} \binom{m}{g} \frac{Np}{m}^g (1 - Np/m)^{m-g}$$

(7)

where $P_C$ represents the nonoverlapping energy gap and also the sum of the probabilities of the presence of $e^-$s in the CB within the $g$ energy gaps. In eq 6, “g” takes all integer values in the interval $[k, m]$, where $k \leq m$. Therefore, considering the different conditions, three formalized models are presented for interpretation of $e^-$ transport across Fe/Ti LDH.

Model 1: When $m \to \infty$ (i.e., the energy gap is sufficiently large) and $p_r \to 0$ (i.e., the probability of availability of electron in CB is very small and hence $Np_r$ would also be small), for minimum number of $e^-$s at CB, $k = 1$. Hence, eq 7 has been approximated using Poisson distribution with parameter $(Np, e^*)$ as

$$\lim_{m \to \infty} P_C = \lim_{m \to \infty} \sum_{g=k}^{m} \binom{m}{g} \frac{Np}{m}^g e^{-Np} \to 1 - e^{-Np}$$

$$= 1 - e^{-e^*/\bar{E}} = P_{\text{expo}}(e^*)$$

(8)

where $P_{\text{expo}}(e^*)$ represents the cumulative density function of exponential energy gap with parameter $Np_r = 1/\bar{E}$.

Model 2: When $m$ is very large, i.e., $m \to \infty$, but neither of $p_r^*$; where $p_r^* = \binom{Np}{m}$, and $(1 - p_r^*)$ are close to zero, the binomial distribution could be approximated by Gaussian distribution with mean $\mu = Np_r^*$ and variance $\sigma^2 = Np_r^*(1 - p_r^*)$. When $m$ is very large and large energy gaps are expected to exist within the LDH between the VB and the CB, eq 7 can be approximated using Stirling’s approximation as

$$P(g) = \rho e^{-(g-Np\bar{E})^2/2Ng^2}$$

(9)

where $\rho$ represents the normality constant and $\bar{E} = 1/Np_r$ is the mean value of the statistical energy gap. Since the energy gap $g$ is sufficiently large, the summation (7) could be changed to the integral form as

$$dP(g) = P(g)dg = \frac{1}{\sqrt{2\pi Np_g^2}} e^{-(g-Np\bar{E})^2/2Ng^2}dg$$

(10)

The mean numbers of $e^-$s in the CB for the prefixed energy $\bar{E}$ is represented by $Np_r$ (a constant) and $g = \lceil Np_r e^* \rceil$ (the greatest integer part of $Np_r e^*$), and eq 10 for the given $Np_r$ and the statistical energy gap $g$ could be approximated as Gaussian distribution with $\mu = \bar{E}$ and $\sigma^2 = \bar{E}/Np_r$, and the density function for energy $(\bar{E})$ would be represented as $f(\bar{E}) = 1/\sqrt{2\pi \sigma^2} e^{-(\bar{E}^2/2\sigma^2)}$

$$f(\bar{E}) = \frac{1}{\sqrt{2\pi \sigma^2}} e^{-(\bar{E}^2/2\sigma^2)}$$

(11)

Model 3: If medium number of $e^-$s are transferred $(Np_r)$ to CB, then $e^-$ distribution would neither be determined by Gaussian method nor by exponential model. In this situation, the mixture of these two distributions could be considered as an alternative model. The analytical expression for mixed Gaussian--exponential density function is considered to be a convex combination of Gaussian and exponential distributions, which is of the form

$$f_{\text{mix}}(\bar{E}) = \alpha f_{\text{expo}}(\bar{E}) + (1 - \alpha)f_{\text{gauss}}(\bar{E})$$

$$f_{\text{mix}}(\bar{E}) = \alpha \frac{1}{\sqrt{2\pi \sigma^2}} e^{-(\bar{E}^2/2\sigma^2)} + (1 - \alpha) \frac{1}{\sqrt{2\pi \sigma^2}} e^{-(\bar{E}^2/2\sigma^2)}$$

(12)

where $\alpha$ is the incidence probability. The threshold energy required for $e^-$ transport across the band gap of the LDH (from VB to CB) at a given temperature $T$ is represented by $E_C$. Hence, if the supplied energy $E > E_C$, then the $e^-$ movement from VB to CB is possible. Moreover, $E_C$ is considered to be fixed for an LDH or any semiconductor system for all temperatures. Hence, probability $\theta(T,e^*)$ of $e^-$ transfer from VB to CB at temperature $T$ and energy $E$, such that $E > E_C = e_C$ has been obtained using Fermi–Dirac statistics using the equation

$$\pi(T, e^*) = f(E = e^*/T, E_C = e_C) = 1 + e^{-(e^* - e)/k_bT}$$

(14)

where $k_b$ is the Boltzmann constant, $E_C = e_C$ represents the conduction band energy, and $T$ represents temperature in Kelvin scale. The approximation for $\theta(T)$ given by Fermi–Dirac statics $\pi(T, e^*)$ (eq 14), is presented in Figure 8.

The analytical expressions of the models for the statistical energy gap based on exponential, Gaussian, and mixed Gaussian–exponential density functions, based on given $E_C$ and $T$, are of the form

$$f_{\text{expo}}(\bar{E}, E_C = e_C) = Np_r(T, e_C) e^{-(Np_r(T, e_C))}$$

$$f_{\text{gauss}}(\bar{E}, E_C = e_C)$$

$$Np_r(T, e_C) = \sqrt{\frac{2\pi \sigma^2}{e^*}} e^{-(Np_r(T, e_C)) \left[1 - \frac{1}{Np_r(T, e_C)}\right]^2}$$

(15)

(16)

Figure 8. Probability of electron transferred from VB to CB for temperature $T$ and energy $E > E_C$.
The pattern of energy density is approximated under different models through the Monte Carlo technique. The Monte Carlo process provides an empirical summary of the density using the simulated values, which shares the same distributional properties. To understand the concept of $e^-$ transport across the semiconductor LDH under different suggested models, it is assumed that the defects/traps are distributed according to the choice of the model. The pattern of distribution of the number of traps on different energy and temperature scales within the LDH are presented herein. Let $N_t (= 1.0 \times 10^6)$ denote the number of traps, assumed to be distributed uniformly in a $100 \times 100 \times 100$ cubic box, with periodic boundary condition being considered; $k_B (= 1.38 \times 10^{-23}$ J K$^{-1}$) represents Boltzmann constant; $T_o$ is the standard temperature (in Kelvin); and $E_C$ denotes the conduction band energy of the LDH. $E_C$ defines the minimum amount of energy required to transfer an electron from VB to CB. To incorporate the situation considered for model 1, the energy gap has been assumed to be sufficiently large and therefore the probability of availability of electron in CB is considered to be very small. This is possible only if $E_C$ is comparatively very low, and for consideration of this extreme situation, it is assumed that $E_C = 0$ (unknown). On the other hand, to incorporate a more realistic condition, where $E_C$ has been calculated on the basis of the parameters under the experimental setup, it is denoted as $E_C$ (calculated). In the present study, the density of the LDH has been approximated for both the conditions and the pattern of density is approximated for conduction band energy ($E_C$) and valence band energy ($E_V$), which has been calculated using the following equations reported by Zhang et al.:

$$E_C = -\chi_{\text{oxide}} (\text{eV}) + \frac{1}{2}E_g + 0.059(PZZP - \text{pH}^*)$$ (18)

$$E_V = -\chi_{\text{oxide}} (\text{eV}) - \frac{1}{2}E_g + 0.059(PZZP - \text{pH}^*)$$ (19)

where $\chi$ and $E_g$ represent the absolute electronegativity and band gap energy of the LDH, respectively; PZZP is the pH (7.2) at which Fe/Ti LDH exhibits zero $\zeta$-potential (Supporting Information); and pH* is the experimentally observed pH 7.2, in which the surface of the material remains neutral. The $\chi_{\text{oxide}} (\text{eV})$ value was calculated by using the following set of equations:

$$\chi (\text{eV; elements}) = \frac{E_{\text{IE}} + E_{\text{EA}}}{2}$$ (20)

$$\chi_{\text{oxide}} (\text{eV; } A_xB_yO_z) = \left(\chi^x_{A} \chi^y_{B} \chi^z_{O}\right)^{1/(x+y+z)}$$ (21)

where $\chi$ (eV; elements) is the electronegativity of elements in eV scale; $E_{\text{IE}}$ and $E_{\text{EA}}$ 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 Fe$_{0.67}$Ti$_{0.33}$O$_{1.55}$ (Supporting Information), and for this mixed oxide, $\chi_{\text{oxide}} (\text{eV})$ is calculated as 5.77 eV (S4; Figure 9. Trap energies are distributed according to exponential (A, C) and Gaussian (B, D) densities for given temperature $T$ and energy $E > E_C = 0$ and $E_C = -4.45$ eV.)
Supporting Information). In this study, the $E_C$ and $E_V$ values are calculated by using these equations, which are used to have the patterns of energy density under different models through the Monte Carlo technique. The values of $E_C$ and $E_V$ are calculated to be $-4.45$ and $-7.10$ eV, respectively, for Fe/Ti LDH.32-35

The patterns of trap density for Fe/Ti LDH under the three different models have been approximated under two sets of conditions $E_C = 0$ and $-4.45$ eV, using Monte Carlo simulations, and are shown in Figures 9–11. It depicts the distributional pattern of the trap densities with changes in the energy level (in eV) and temperature (in Kelvin) for both the scenarios under $E_C = 0$ and $-4.45$ eV, respectively. At $E_C = 0$ (Figure 9A), the distribution of trap numbers, based on model 1, showed that with increase in temperature and energy below $\sim 0.45$ eV, the trap numbers show an increasing pattern, and above that energy, it starts decreasing and is observed to be stabilized around $4 \times 10^5$. Under model 2, for $E_C = 0$, the trap numbers (Figure 9B) show an increasing trend with increase in temperature and energy. When $E_C = -4.45$ eV (Figure 9C), the trap number based on model 1 shows a decreasing trend; on the other hand, Figure 9D, based on model 2, shows an increasing trend in trap numbers with increase in temperature and energy.

Figures 10 and 11 depicts the changing pattern in trap numbers with changes in temperature and energy in model 3 at $E_C = 0$ and $-4.45$ eV, respectively, for different values of incidence probability, say $\alpha$. Here, as $\alpha$, temperature, and energy below $\sim 0.45$ eV increase, the trap numbers show an increasing trend (Figure 10), and above $0.45$ eV energy level, the trap numbers show a decreasing pattern. In Figure 11, where $E_C = -4.45$ eV, it is observed that with increase in $\alpha$ and temperature, the trap numbers increase toward lower energy levels.

4. CONCLUSIONS

Thus, Fe/Ti LDH exhibited hexagonal morphology with narrow band gap within the layered framework. The occurrence of $e^-$ transport across the semiconducting LDH has been confirmed using UV-visible diffuse reflectance spectroscopy analysis. Accordingly, empirical models based on exponential, Gaussian, and the mixed Gauss–exponential distributions successfully justified the concept of $e^-$ transport across the band gap of the LDH nanomaterial. Fermi–Dirac statistics successfully estimated the probability of transfer of $e^-$ from VB to CB at a given temperature and for given energy. The simulated results based on model 1 reveals that exponential distribution to be appropriate under the conditions where the energy gap is sufficiently large and the probability of availability of electron in CB is very small. Moreover, the present work also reveals the importance of Gaussian (when the energy gap is sufficiently large and probability of availability of electron is not close to zero) and mixed Gauss–exponential models (when the medium number of electrons are transferred to the CB) for interpretation of the $e^-$ transport phenomenon across the LDHs.

5. EXPERIMENTAL SECTION

5.1. Materials. Fe(NO$_3$)$_3$·9H$_2$O, TiCl$_4$, and urea of analytical grade are used as precursors for Fe/Ti LDH synthesis, acquired from Merck Chemicals Co. Decarbonated water has been used during the experimental processes.
5.2. Fe/Ti LDH Synthesis. Fe/Ti LDH has been synthesized hydrothermally using Fe(NO$_3$)$_3$·9H$_2$O, TiCl$_4$, and urea. The typical hydrothermal synthesis involves mixing of 11.169 g of Fe(NO$_3$)$_3$·9H$_2$O, 1.1 mL of TiCl$_4$, and 3.0 g of urea together in 100 mL of decarbonated water at room temperature (303.15 K) with vigorous stirring for 2 h followed by aging in a Teflon-lined autoclave at 413.15 K for 36 h. The brick-red crystalline product was extracted with centrifugation, washed three times with water, and dried at 353.15 K for 6 h.

5.3. Characterizations. Powder X-ray diffraction (XRD) pattern of Fe/Ti LDH was carried out using a PANalytical X-Pert PRO diffractometer equipped with monochromatic Cu Kα X-ray radiation (λ = 0.15418 nm) at 25 mA and 35 kV with a scanning rate of 4° min$^{-1}$ along the 2θ range of 5–80°. The morphological study and the elemental composition of Fe/Ti LDH were evaluated with Zeiss Gemini SEM (5 kV)/EDX (15 kV). Gold coating of the specimen was done at ∼6 nm min$^{-1}$ (at a pressure of 7 × 10$^{-2}$ Pa and a current 20 mA) with Quorum (Q 150R ES). Atomic force microscopy (Oxford Instruments; Cypher Asylum Research, equipped with ARC2 controller) was employed in noncontact tapping mode using a Si tip of 10 nm radius to obtain information about the surface topography of Fe/Ti LDH. The Fe/Ti LDH sample is dispersed in ethanol (EtOH) by ultrasonication for ~5 min, and the dispersion was spread over a glass slide (10 × 10 mm$^2$) with a micropipette and then allowed to dry in air. Fourier transform infrared (FT-IR) spectroscopy was conducted with a Shimadzu FT-IR 3000 spectrometer. The LDH sample was mixed with KBr in weight ratio 1:100 and compressed to form pellets for analysis. UV–visible diffuse reflectance spectroscopy of the LDH sample was conducted with a Hitachi U4100 spectrometer, equipped with integrating sphere attachment having BaSO$_4$ background.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01345.

X-ray diffraction lattice parameters and AFM results; PZZP of Fe/Ti LDH; determination of the formula of the mixed oxide Fe$_x$Ti$_{(1-x)}$O$_y$; and calculation of absolute electronegativity of Fe$_{0.67}$Ti$_{0.33}$O$_{1.55}$ (PDF)

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Notes
The authors declare no competing financial interest.
The simulations were carried using R-software version-3.4.1.

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