PHOTOLUMINESCENCE SPECTROSCOPIC STUDIES OF MN2O3/CO3O4-GluCOSE/LACTOSE COMPLEXES

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1. INTRODUCTION

Metal oxide nanomaterials have increasingly interfered in almost all technologies. This is believed to be due to the novel properties of materials when diminished to the nanoscale and assembled in unique morphologies (Abdolmohammad-Zadeh et al., 2020). Among the various metal oxides, \( \text{Mn}_2\text{O}_3 \) and \( \text{Co}_3\text{O}_4 \) nanoparticles have attracted research interests that thrived into preparing them via various techniques and widely using them in several applications, including wastewater treatment photocatalytic applications, microwave absorption, supercapacitors, sensors, MRI, biomedicine, antibacterial, antioxidant and enzyme inhibition activity (Can et al., 2020; Deka et al., 2020; Jiang et al., 2020b; Khalil et al., 2020; Kbra et al., 2020; Letsholathebe et al., 2020; P. Liu et al., 2020; Shaheen & Ahmad, 2020; X. Wei et al., 2020; Xie et al., 2020; Yang et al., 2020; C. Zhang et al., 2020).

Nanomaterials have proven their profound influence in the sector of enzyme-free biosensors. The distinguishable properties of materials at the nanoscale regime, especially biocompatibility and high activity, miniaturized the bio-sensing devices along with enhancing their detection sensitivity and specificity (Hou et al., 2018; X. Zhang et al., 2009). The \( \text{Mn}_2\text{O}_3 \) and \( \text{Co}_3\text{O}_4 \) nanoparticles belong to the metal oxides that are considered beneficial for the non-enzymatic glucose determination, utilized as electro-catalysts for glucose oxidation (Ahmad et al., 2020). Vukojevic et al. (Vukojević et al., 2018) prepared disposal glucose biosensors using \( \text{MnO}_2 \) nanoparticles on graphene nanoribbons. A synergetic effect of manganese dioxide decorated by graphene nanoribbons increased the characteristics of the electrode surface. Kumar et al. (Kumar et al., 2017) studied the electrochemical detection of p-nitrophenol using \( \text{MnO}_2 \) nanoparticles of different sizes. \( \text{MnO} \) nanoparticles were found useful for sensing harmful chemicals and in various in vivo biological applications. Moreover, a recent study by Waqas et al. (Waqas et al., 2020) was conducted on Pd-Mn nanocatalyst supported on reduced graphene oxide (rGO) for the construction of non-enzymatic electrochemical sensor for glucose or even for any other analyte. Enhanced electrochemical efficacy of Pd-Mn/rGO electrocatalyst was explained by abundant electrocatalytic active sites formed during the Pd-Mn alloying and the electron transport ability of rGO. On the other hand, Li et al. (S.-J. Li et al., 2014) studied the performance of \( \text{Co}_3\text{O}_4 \) nanoparticles/graphene oxide modified electrodes in amperometric enzymatic-free glucose biosensors. The developed biosensor showed a short response time (less than 5 s), high sensitivity of 79.3 \( \mu\text{A} \text{mM}^{-1} \text{cm}^{-2} \), and good selectivity. Also, Zheng et al. (Zheng et al., 2014) studied the reduced graphene oxide and \( \text{Co}_3\text{O}_4 \) nanocomposites for non-enzymatic glucose sensors. Superior electrochemical activity towards the oxidation of glucose was noticed. After Kang et al. (Kang et al., 2019) offered a detailed study on the key role of L-lysine on the synthesis of highly porous \( \text{Co}_3\text{O}_4 \) nanoplates via the hydrothermal method, the performance of the prepared \( \text{Co}_3\text{O}_4 \) nanoplates towards non-enzymatic glucose sensing was investigated. The glucose sensors fabricated by the obtained porous \( \text{Co}_3\text{O}_4 \) nanoplates exhibited high performance represented by several factors, including fast response time (within 5 s) and good stability at low applied potential (0.38 V vs. Ag/AgCl).

Recently, research interest has increased in the field of nano-fluorescent biosensors due to their high sensitivity, simple, fast, low cost, and low background signals (Bhardwaj et al., 2017; Hou et al., 2018). Chen et al. (C. Chen et al., 2018) reported a study on glucose fluorescent biosensor, based on water-soluble and pH-responsive silicon nanodots. Glucose in human serum samples was detected with high sensitivity and selectivity. Billingsley et al. (Billingsley et al., 2010) designed fluorescent nanosensors based on ion-selective optodes capable of detecting small molecules.

Previously, we investigated NiO nanoparticles, prepared via coprecipitation method, and their interactions with both glucose and lactose (Abdallah et al., 2019). NiO nanoparticles were utilized for lactose non-enzymatic biosensors, as it was implied from the UV absorption and fluorescence spectroscopic studies. The interactions of lactose-NiO nanoparticles were found to be stronger than that of glucose-NiO ones. In the present work, we investigate \( \text{Mn}_2\text{O}_3 \) and \( \text{Co}_3\text{O}_4 \) nanoparticles, prepared by the chemical coprecipitation method. Then, we study the photoluminescence interactions between the \( \text{Mn}_2\text{O}_3/\text{Co}_3\text{O}_4 \)- glucose/lactose complexes to recognize the interaction of each one of these nanoparticles with glucose and lactose.

A comparative study is implemented between the \( \text{Mn}_2\text{O}_3/\text{Co}_3\text{O}_4 \) nanoparticles of the present study and the NiO nanoparticles of the previous study with glucose and lactose to perceive the metal oxide that is better to be utilized in glucose and lactose non-enzymatic biosensors.
2. EXPERIMENTAL ROUTE

2.1 Nanoparticles’ Preparation

The prepared metal oxide, Mn$_2$O$_3$ and Co$_3$O$_4$, nanoparticles were synthesized by the chemical coprecipitation method. Starting from the preparation of 1 M chloride solutions, the convenient stoichiometry of the salt chlorides (MnCl$_2$·4H$_2$O and CoCl$_2$·6H$_2$O) was dispersed in distilled water. Thereafter, titration with 4 and 3 M Sodium Hydroxide NaOH, was carried out to the MnCl$_2$ and CoCl$_2$ solutions, respectively, to reach a basic medium of pH 13. This high pH induces more hydroxyl ions that ensure suitable nucleation and growth for the prepared samples (Palanisamy & Raichur, 2009). Then, the obtained hydroxide solutions (Mn(OH)$_2$ and Co(OH)$_2$) were heated at 343 K for 2 h and 333 K for 4 h, respectively. The heated solutions were set to cool down, and then they were filtered and washed thoroughly by distilled water to reach a neutral pH (i.e., pH=7). The resultant precipitates were dried at 373 K overnight, ground, and then calcined. Specifically, the Mn$_2$O$_3$ were calcined at 823 K for 6 h and the Co$_3$O$_4$ were calcined at 973 K for 4 h. Finally, the powders were ball milled, applying a 5:1 weight ratio of the balls to powders, for 20 min with a speed of 400 rpm.

2.2 Characterization Techniques

The structural properties of the prepared metal oxides (Mn$_2$O$_3$ and Co$_3$O$_4$) were investigated by X-Ray Diffraction (XRD) of Bruker D8 focus and Cu–K$_\alpha$ radiation source (λ = 1.54056 Å). The morphology of the prepared metal oxides was tested by Transmission Electron Microscope (TEM), JEM 100CX, having a resolution of 0.1 nm, operated at 80 kV. Moreover, Energy Dispersive X-ray (EDX), EDAX-ZAF, operating at 20 kV, and Fourier Transform Infrared (FTIR) spectroscopy, Nicolet iS5 FTIR spectrometer, were used to gain insights about the elemental composition and the vibrational modes present in the samples. The optical properties of the samples were studied by dissolving 0.01 g of the nanoparticles (Mn$_2$O$_3$ and Co$_3$O$_4$) in 50 mL of ethanol, followed by 5 min of sonication. The samples’ absorbance, energy gap, Urbach energy, and steepness parameter were determined from the absorbance spectra of the prepared solutions, measured at room temperature by Ultraviolet-visible (UV-vis) spectroscopy, V-670. The Vibrating Sample Magnetometer (VSM), Lakeshore 7410, was utilized to explore the hysteresis loop of the prepared oxides, from which the remnant magnetization, coercivity, saturation magnetization, and squareness were evaluated.

2.3 Photoluminescence Investigations

The prepared metal oxides (Mn$_2$O$_3$ and Co$_3$O$_4$) were then mixed, in different concentrations, with 1×10$^{-4}$ M of glucose and lactose to study the change in their photoluminescence activity. These interactions were held in a phosphate buffer medium of concentration 0.1 M and pH 6.5. The photoluminescence (PL) spectroscopy, FP-8300 spectrofluorometer accompanied by a Xenon (Xe) lamp, was used for this study with a 273 nm excitation wavelength.

3. RESULTS AND DISCUSSIONS

3.1 Structural Analysis

Error! Reference source not found. reveals the XRD patterns, with the corresponding (hkl) Miller indices, for (a) Mn$_2$O$_3$ and (b) Co$_3$O$_4$ nanoparticles. Both spectra are assigned to the cubic phase of the Mn$_2$O$_3$ and Co$_3$O$_4$ nanoparticles with no extra phases or impurities. Similar results were reported in the literature (Ahmed et al., 2020; Anuradha & Raji, 2019; Feng et al., 2020; Gajendiran et al., 2020; Iqbal et al., 2020a; Jiang et al., 2020a; Z. Li et al., 2020; Mahani et al., 2020; Teli et al., 2020; G. Wei et al., 2019).

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The lattice parameter \( (a) \) and the crystallite size \( (D) \) were obtained from Bragg’s law (Eq. (1)) and Debye Scherrer’s formula (Eq. (2)), respectively (Timoumi et al., 2020):

\[
a = d_{hlk} \sqrt{h^2 + k^2 + l^2},
\]

\[
D = \frac{k \lambda}{\beta \cos \theta},
\]

where, \( d_{hlk} \) is the interplanar distance between the adjacent planes, \( k = 0.9 \) is a shape factor, \( \beta \) is the full-width at half maximum, and \( \theta \) is the glancing angle. The values of \( (a) \) and \( (D) \) are listed in Table 1. Moreover, the X-ray density \( (\rho_x) \), the dislocation density \( (\delta) \), and the specific surface area \( (SSA) \) were calculated and collected in Table 1, according to the following equations (Bharati et al., 2020; Jabbar et al., 2020):

\[
\rho_x = \frac{4M}{N_A a},
\]

\[
\delta = \frac{1}{D_{	ext{XRD}}^2},
\]

\[
SSA = \frac{SA}{M} = \frac{SA}{\rho_x \times V},
\]

where, \( M \) is the molecular weight, \( N_A \) is Avogadro’s number, \( SA \) is the surface area and \( V \) is the volume of the crystal. It is noticed that \( \text{Mn}_2\text{O}_3 \) has larger \( SSA \) than that of \( \text{Co}_3\text{O}_4 \) nanoparticles. Accordingly, since the catalytic activities are enhanced with larger \( SSA \) (Cui et al., 2019; Pedireddy et al., 2014), \( \text{Mn}_2\text{O}_3 \) may be more applicable than \( \text{Co}_3\text{O}_4 \) nanoparticles for non-enzymatic biosensors.

![XRD patterns for (a) Mn$_2$O$_3$ and (b) Co$_3$O$_4$ nanoparticles](image-url)
Table 1: The structural parameters of the Mn$_2$O$_3$ and Co$_3$O$_4$ nanoparticles

<table>
<thead>
<tr>
<th></th>
<th>Mn$_2$O$_3$</th>
<th>Co$_3$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>9.4169</td>
<td>8.091</td>
</tr>
<tr>
<td>$D$ (nm)</td>
<td>65.910</td>
<td>58.000</td>
</tr>
<tr>
<td>$\rho \times 10^3$ (kg / m$^3$)</td>
<td>1.256</td>
<td>3.019</td>
</tr>
<tr>
<td>$\delta \times 10^4$ (m$^2$)</td>
<td>2.302</td>
<td>2.973</td>
</tr>
<tr>
<td>SSA $\times 10^4$ (m$^2$ / kg)</td>
<td>1.281</td>
<td>0.571</td>
</tr>
<tr>
<td>$D_p$ (nm)</td>
<td>65.170</td>
<td>73.850</td>
</tr>
<tr>
<td>$I$</td>
<td>0.989</td>
<td>1.273</td>
</tr>
</tbody>
</table>

3.2 Morphological Analysis

The TEM images, shown in Error! Reference source not found. for the (a) Mn$_2$O$_3$ and (b) Co$_3$O$_4$ nanoparticles, depict highly agglomerated particles. The Mn$_2$O$_3$ nanoparticles exhibit a cubic nature, while the Co$_3$O$_4$ nanoparticles reveal spherical particles. The particle size distributions are drawn in Fig. 2 for (c) Mn$_2$O$_3$ and (d) Co$_3$O$_4$ nanoparticles, from which the average grain size ($D_p$) was computed and listed in Table 1.

Moreover, the crystallinity index ($I$), which is the ratio of the average grain size, computed from TEM images to the crystallite size, obtained from XRD patterns, is calculated and listed in Table 1 (Sahai & Goswami, 2014). It was found that both nanoparticles have crystallinity index values ~ 1, accounting for the monocristalline nature of the prepared nanoparticles. Notice that the Co3O4 nanoparticles have a higher crystallinity index than Mn2O3, indicating the higher degree of agglomeration in Co3O4 nanoparticles (CNhopade et al., 2018). Such a crystallinity index can be explained by the agglomeration that most probably occurs during the preparation of the sample for the TEM measurements (Hafeez et al., 2020). Moreover, the agglomeration is ascribed to Ostwald’s ripening process, where the formation of nanoparticles tends to reduce free energy (Voorhees, 1985). Thus, bigger and agglomerated nanoparticles are formed by the coalescence of smaller nanoparticles (Amiar Rodin et al., 2020).

![TEM images for (a) Mn$_2$O$_3$ and (b) Co$_3$O$_4$ nanoparticles with their particle size distribution histograms (c) and (d)](Fig.2: TEM images for (a) Mn$_2$O$_3$ and (b) Co$_3$O$_4$ nanoparticles with their particle size distribution histograms (c) and (d))
3.3 Vibrational bands and Elemental Composition

Error! Reference source not found. reveals the FTIR spectra of the investigated (a) Mn$_2$O$_3$ and (b) Co$_3$O$_4$ nanoparticles. In the group frequency region (region I) of both spectra, the presence of adsorbed water molecules and/or increased humidity is detected by the two peak ranges appearing at about 3440 cm$^{-1}$ and 1645 cm$^{-1}$. Moreover, in the fingerprint region (region II), the two main peaks corresponding to the absorption bands of Mn$_2$O$_3$ and Co$_3$O$_4$ nanoparticles appear, identifying their successful formation. Specifically, the Mn$_2$O$_3$ spectrum establishes the two peaks at 610.36 and 530.33 cm$^{-1}$, ascribed to the stretching vibrations of Mn–O and Mn–O–Mn bonds, respectively. Besides, the peaks of the Co$_3$O$_4$ spectrum at 664 and 572 cm$^{-1}$ are indicative of the stretching vibrational mode of Co$^{2+}$–O and Co$^{3+}$–O bonds, respectively. The same results were reported in the literature (H. Chen et al., 2020; Jassem et al., 2019; Medina et al., 2020; Son et al., 2019; Su et al., 2020).

The EDX graphs are represented in Error! Reference source not found. for (a) Mn2O3 and (b) Co3O4 nanoparticles with the corresponding elemental compositions listed in Table 2.

Fig.3: FTIR spectra for (a) Mn$_2$O$_3$ and (b) Co$_3$O$_4$ nanoparticles

Fig.4: EDX spectra for (a) Mn$_2$O$_3$ and (b) Co$_3$O$_4$ nanoparticles
Apparent peaks of oxygen (O), manganese (Mn), and cobalt (Co) are observed, assuring the purity of the prepared samples. The carbon signal emerges from the mesh coating of the instrumental grid support (B. Liu et al., 2010).

Table 2: The elemental compositions of the Mn$_2$O$_3$ and Co$_3$O$_4$ nanoparticles

<table>
<thead>
<tr>
<th></th>
<th>Mn$_2$O$_3$</th>
<th>Co$_3$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. %</td>
<td>80.44</td>
<td>60.96</td>
</tr>
<tr>
<td>At. %</td>
<td>54.50</td>
<td>28.31</td>
</tr>
</tbody>
</table>

3.4 Optical Analysis

The absorbance spectra for (a) Mn$_2$O$_3$ and (b) Co$_3$O$_4$ nanoparticles, investigated by UV-vis spectroscopy, are shown in Fig. 5. For Mn$_2$O$_3$ nanoparticles, two small peaks appear in the ultraviolet range (340 nm) and the visible range (553 nm), as clarified by the spectrum’s fitting displayed in the inset of Fig. 5 (a). On the other hand, the absorbance spectrum of the Co$_3$O$_4$ nanoparticles shows two obvious peaks at 278 and 537 nm. These peaks are ascribed to the charge transfer between the Co$^{2+}$–O$^2-$ and Co$^{3+}$–O$^2-$ ions localized at the tetrahedral and octahedral sites, respectively (Saravanakumar et al., 2018; Vennela et al., 2019).

Moreover, Tauc plots, shown in Fig. 6, were concerned to determine the energy gap ($E_g$) of the samples according to the following equation (Phan et al., 2019; Ravi Dhas et al., 2015):

$$\frac{(a\lambda)^n}{\lambda} = \alpha_0 (h\nu - E_g),$$

where $a\lambda$ is the measured absorbance, $L$ is the samples’ thickness, $n$ is an exponent related to the types of the transitions, $\alpha_0$ is a material-dependent constant, and $h\nu$ is the energy. Accordingly, $E_g$ was calculated for the direct allowed transitions ($n=1/2$) for both oxides and listed in Table 3. Mn$_2$O$_3$ nanoparticles have a small $E_g$, and Co$_3$O$_4$ has two energy gaps emerging from the two different charge transfer processes. However, the energy gap is highly affected by lattice distortions, non-stoichiometry, quantum confinement effect, and structural disorders.
The Urbach energy (Eu) accounts for all possible defects, as it describes the width of the localized states in the bandgap (Turgut & Sönmez, 2014). Eu is computed from the slope of the logarithmic absorbance plot versus the energy, shown in the insets of Fig. 6, according to the following equation (Kocyigit, 2018):

\[
\log \alpha = \beta + \frac{h\nu}{E_u},
\]

where $\beta$ is a material-dependent factor. Also, the steepness parameter ($\sigma$), describes the harmonic interaction between the longitudinal optical phonons and excitons that describes the steepness of the exponential increase before the $E_g$. $\sigma$ was discussed according to the following equation (Kocyigit, 2018; Turgut & Sönmez, 2014):

\[
\sigma = \frac{k_B T}{E_u}.
\]

The obtained values of $E_u$ and $\sigma$ are listed in Table 3. Co$_3$O$_4$ nanoparticles possess higher Urbach energy than Mn$_2$O$_3$ nanoparticles. This means that Co$_3$O$_4$ nanoparticles encounter more defects and disorders in their bonding that may arise due to the excitons and phonons of the multi-charges present in the structure (Ebrahimi et al., 2019).

<table>
<thead>
<tr>
<th>Table 3: The optical parameters of the Mn$_2$O$_3$ and Co$_3$O$_4$ nanoparticles</th>
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<tbody>
<tr>
<td>$E_{\alpha}$ (eV)</td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>$E_{\alpha}$ (eV)</td>
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<tr>
<td>$E_{\alpha}$ (eV)</td>
</tr>
<tr>
<td>$E_{\alpha}$ (eV)</td>
</tr>
<tr>
<td>$\sigma \times 10^{-3}$</td>
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</table>

### 3.5 Magnetic Analysis

The room temperature hysteresis loops of the investigated (a) Mn$_2$O$_3$ and (b) Co$_3$O$_4$ are traced in Error! Reference source not found.. Mn$_2$O$_3$ exhibits an antiferromagnetic behavior; however, Co$_3$O$_4$ follows a weak ferromagnetic one. Similar results were reported in the literature (Anandha Babu et al., 2015; Pugazhavadi et al., 2013; Zhu et al., 2008).
The remnant magnetization ($M_r$) and coercivity ($H_c$) were extracted from the loops and tabulated in Table 4. Furthermore, the saturation magnetization ($M_s$) was not reached even after applying a magnetic field of 20 kOe. Accordingly, the law of approach to saturation was implemented to determine the $M_s$, given by the following equation (Ghasemi et al., 2020; Singh et al., 2020):

\[ M = M_s \left( 1 - \frac{a}{H} - \frac{b}{H^2} \right) + \chi H, \]

where $M$ is the magnetization, $H$ is the applied field, $a$ is a constant related to structural defects and/or micro-stress, $b$ is a constant related to anisotropy, and $\chi$ is the susceptibility at high field. However, below Curie temperature and high field limit, $a/H$ and $\chi H$ terms can be neglected (Selvaraj et al., 2020). Thus, equation (9) is reduced to:

\[ M = M_s (1 - \frac{b}{H^2}). \]

Therefore, the linear fit of $M$ versus $H^2$, shown in Error! Reference source not found. Figure 7: M-H loop for (a) Mn$_2$O$_3$ and (b) Co$_3$O$_4$ nanoparticles with corresponding insets at low field region

<table>
<thead>
<tr>
<th></th>
<th>Mn$_2$O$_3$</th>
<th>Co$_3$O$_4$</th>
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<tbody>
<tr>
<td>$M_r \times 10^3$ (emu/g)</td>
<td>73.597</td>
<td>4.370</td>
</tr>
<tr>
<td>$H_c$ (Oe)</td>
<td>82.041</td>
<td>47.862</td>
</tr>
<tr>
<td>$M_s$ (emu/g)</td>
<td>2.435</td>
<td>0.813</td>
</tr>
<tr>
<td>$S \times 10^3$</td>
<td>30.225</td>
<td>5.375</td>
</tr>
</tbody>
</table>
The $M_S$ values, listed in Table 4, signify that $\text{Mn}_2\text{O}_3$ has the highest value owing to the fact that the magnetic moment of manganese ($\sim 5\mu_B$) is higher than that of cobalt in tetrahedral site ($\text{Co}^{2+} (\sim 4.14\mu_B)$), regardless of the diamagnetic $\text{Co}^{3+}$ in the octahedral site (Moro et al., 2013; Pugazhvadivu et al., 2013). This makes $\text{Mn}_2\text{O}_3$ superior to $\text{Co}_3\text{O}_4$, since many biomedical applications require high $M_S$, as bacterial detection, protein purification, tracking of cells, hyperthermia, enzyme immobilization, and drug delivery (Amiri & Shokrollahi, 2013; Anbarasu et al., 2015; Elrefai et al., 2019; Huang & Juang, 2011). Hence, $\text{Mn}_2\text{O}_3$ has a greater potential than $\text{Co}_3\text{O}_4$ nanoparticles to be investigated in further applications. Moreover, the squareness ($S$) was estimated according to the following equation (Hessien et al., 2020; Shumskaya et al., 2020):

\[ S = \frac{M_f}{M_S}. \]

The $S$-values are reported in Table 4, and it is noticed that $\text{Mn}_2\text{O}_3$ nanoparticles have larger value than $\text{Co}_3\text{O}_4$ nanoparticles due to its larger $M_f$. Also, the squareness values for both $\text{Mn}_2\text{O}_3$ and $\text{Co}_3\text{O}_4$ nanoparticles are less than 0.5, suggesting that the nanoparticles are related to multi-domain structure, following the Stoner-Wohlfarth model (Amiar Rodin et al., 2020).

### 3.6 Photoluminescence Analysis for Glucose and Lactose/ Nanoparticles Interactions

The photoluminescence spectra, shown in Error! Reference source not found., were measured at room temperature for different concentrations of $\text{Mn}_2\text{O}_3$ and $\text{Co}_3\text{O}_4$ nanoparticles ($1\times10^{-4}$ M – $10\times10^{-4}$ M) with a constant concentration of glucose and lactose ($1\times10^{-4}$ M) dissolved in a phosphate buffer medium. Upon addition of $\text{Mn}_2\text{O}_3$ and $\text{Co}_3\text{O}_4$ nanoparticles to glucose and lactose in increased concentrations, the photoluminescence peak in the range of 300-302 nm increased by 34%, 6%, 42%, and 27% for $\text{Mn}_2\text{O}_3$ with glucose, $\text{Co}_3\text{O}_4$ with glucose, $\text{Mn}_2\text{O}_3$ with lactose, and $\text{Co}_3\text{O}_4$ with lactose, respectively. These enhancements of intensities reveal the formation of oxides-carbohydrates complexes ($\text{Mn}_2\text{O}_3$-glucose, $\text{Co}_3\text{O}_4$-glucose, $\text{Mn}_2\text{O}_3$-lactose, and $\text{Co}_3\text{O}_4$-lactose) (Abo El-Maali et al., 2019). The photoluminescence enhancements may be originated from the charge delocalization and the increased rigidity of the oxides ($\text{Mn}_2\text{O}_3$ and $\text{Co}_3\text{O}_4$), by coordination to the carbohydrates (glucose and lactose) (Abo El-Maali et al., 2019; Ji et al., 2013). However, beyond the discussed range, the photoluminescence intensity for $\text{Mn}_2\text{O}_3$ with glucose has flipped, like that; the intensity was reduced upon the concentration addition of $\text{Mn}_2\text{O}_3$ nanoparticles.
Moreover, the photoluminescence intensity of Co$_3$O$_4$ with glucose, in 320-400 nm range, did not follow a normal trend; and the addition of Mn$_2$O$_3$ and Co$_3$O$_4$ nanoparticles to lactose revealed an independent-concentration behavior for the photoluminescence intensity. It can be surmised that the active photoluminescence region for the interactions of Mn$_2$O$_3$ and Co$_3$O$_4$ nanoparticles with glucose and lactose is in the range of 280-320 nm. Furthermore, the modified Stern-Volmer equation was applied to find quantitatively the binding constant ($K$) between the formed complexes (Cao & He, 1998):

\[
\frac{1}{\Delta I} = \frac{1}{K\Delta I'[M]} + \frac{1}{\Delta I'},
\]

where $\Delta I$ represents the change in the photoluminescence intensities between the added nanoparticles and the carbohydrates (glucose and lactose). $\Delta I'$ is a constant related to the formed complex, and $[M]$ represents the different concentrations of the nanoparticles [Mn$_2$O$_3$] and [Co$_3$O$_4$]. Eq. (12) is represented by the double reciprocal plot of Fig. 10, from which $K$ was found and its values are traced in Error! Reference source not found.

Fig.9: Photoluminescence for (a) glucose- Mn$_2$O$_3$ (b) glucose- Co$_3$O$_4$ (c) lactose- Mn$_2$O$_3$ and (d) lactose- Co$_3$O$_4$ complexes
The calculated values were compared to those obtained previously (Abdallah et al., 2019), where the interactions of NiO nanoparticles with both glucose and lactose were investigated. It is noted that the Mn$_2$O$_3$-lactose complex has the highest binding constant amongst the discussed oxides. To elucidate the type of these interactions, the Gibbs energy ($\Delta G^0$) was calculated from the following thermodynamics equation (Paketuryté et al., 2019):

\[
\Delta G^0 = -2.303RT \log K,
\]

where R is the ideal gas constant. The calculated values are traced in Error! Reference source not found. The interactions of the Mn$_2$O$_3$-lactose complex exhibited the smallest $\Delta G^0$ among the three studied oxides (NiO, Mn$_2$O$_3$, and Co$_3$O$_4$) assuring that this complex has the most stable and spontaneous interactions (Mafuwe et al., 2019; Marques et al., 2019).

Fig.10: Double reciprocal plot (a) Mn$_2$O$_3$ and Co$_3$O$_4$with glucose and (b) Mn$_2$O$_3$ and Co$_3$O$_4$with lactose

Fig.11: (a) the binding constant and (b) Gibb’s energy of the formed complexes
4. CONCLUSIONS
As a conclusion, Mn$_2$O$_3$ and Co$_3$O$_4$ nanoparticles were successfully prepared by the chemical coprecipitation route. They exhibited a cubic crystal structure with a crystallite size of 65.91 and 58.00 nm for Mn$_2$O$_3$ and Co$_3$O$_4$ nanoparticles, respectively. Mn$_2$O$_3$ nanoparticles displayed a higher SSA due to the larger crystallite size and a smaller crystallinity index accounting for less agglomeration. Additionally, Mn$_2$O$_3$ nanoparticles acquired smaller Urbach energy, accounting for fewer defects in the sample. This confirmed the presence of less dislocation density in the Mn$_2$O$_3$ nanoparticles, following the XRD results. Besides, Mn$_2$O$_3$ nanoparticles showed a higher saturation magnetization and squareness-parameter arising from its antiferromagnetic nature, confronting the weak ferromagnetic nature of the Co$_3$O$_4$ nanoparticles. These characteristics contributed to higher binding constant, steadier, and spontaneous interactions with glucose and lactose. To sum up, Mn$_2$O$_3$ nanoparticles can be considered viable candidates for glucose and lactose non-enzymatic biosensors.

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