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Lanthanum-Zinc Binary Oxide Nanocomposite with Promising Heterogeneous Catalysis Performance for the Active Conversion of 4-Nitrophenol into 4-Aminophenol

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Abstract: This work intended to enhance the unique and outstanding properties of lanthanum by synthesizing its nanocomposite. A lanthanum-based nanocomposite was prepared by a simple and cost-effective “co-precipitation” method. Lanthanum nitrate (La (NO₃)₃) and zinc nitrate (Zn (NO₃)₂) were used as precursors. The lanthanum/zinc oxide nano composite formed was then calcined at 450 °C for 4 h in order to obtain a fine powder with size in the nano range of 1–100 nm. Characterization of the prepared catalyst was done by ultraviolet/visible spectroscopy, Fourier transform infrared spectroscopy, and photoluminescence. Crystallinity and morphology were found by X-ray diffraction and scanning electron microscopy. The synthesized nanocomposite material was also tested for heterogeneous catalytic applications of 4-nitrophenol (4-NP) reduction into 4-aminophenol (4-AP). It was found to be successful in complete reduction of 4-NP with enhanced catalytic performance.

Keywords: nanocomposite structure; XRD; photoluminescence; rare earth element REE; heterogeneous catalysis

1. Introduction

4-aminophenol (*p*-aminophenol), an imperative intermediate in the manufacturing of multiple pharmaceutical products, mainly including phenacetin, acetanilide, and paracetamol, also has numerous applications in anticorrosion, photography, and lubrication as a dyeing agent [1,2]. Due to its increased demand by pharmacists, the direct catalytic conversion of easily available 4-nitrophenol is the center of huge research [3,4]. Several reduction methods have been reported to date for conversion of 4-nitrophenol into 4-aminophenol [5–7]. The use of precious metals for this catalytic reduction is frequently seen, e.g., Pt, Au, etc. [8,9], involving hydrazine as a reducing agent. However, the discovery and development of more compatible, ecofriendly, and efficient reduction catalysts for this specific reaction is still under research.

Consequently, rare earth metal compounds are being considered by scientists across the globe for investigation of their catalytic performance.

Over the last decade, rare earth metals with nanostructures of size 1–100 nm have been studied by researchers around the world. Owing to the presence of 4f orbital electrons, they have unique properties and offer promising applications in many fields. Their nanostructures are defenseless against compositional or structural effects [10–12]. The electrons in 4f shell orbitals of rare earth metals are continuously shielded by the electrons of 5p and 4d; this feature plays an important role in the catalytic applications of these oxides [13]. The particle size and electronic configuration of metal oxides are interlinked, and the band gaps and energy excitation levels change when the particle size of the metal oxide is reduced [14].

Among nanostructured rare earth metal compounds, Lanthanum metal is an important p-type semiconductor metal, used in numerous fields, such as solar cells [15,16], photocatalysis [17,18], photo detectors [19,20], sensors, light-emitting diodes [21,22], and laser communications [23,24]. Lanthanum oxides with metals is a perovskite type oxide i.e., its ABO_3 type structure makes it special for catalytic applications [25,26]. In addition, Lanthanum metal oxide in powder form, with particle size in nano range of 1–100 nm, exhibits a lot of industrial properties as well. Lanthanum oxides are used in the synthesis of organic catalysts in the field of electrochemistry; it is used as an electrode, and the burning rate of propellants can also be enhanced by lanthanum oxide [27,28].

Moreover, zinc is an important transition metal, due to its feasibility and low cost, and researchers have extensively studied its oxides. Zinc oxide is a non-toxic, highly stable n-type semiconductor having a wide band gap (3.37 eV), which is an attractive feature because it can absorb sufficient amounts of UV light at room temperature [29–31]. Zinc oxides are used in several fields: in solar cells [32,33], super capacitors [34], field effect transistors [35], light-emitting materials [36,37], gas sensors [38], drug delivery [39]; as anticancer [40,41], antibacterial [42], diabetes treatment [43], bio- imaging [44], photocatalysts [45,46], base material for magnetic semiconductors [47], food additive [48], transparent UV- protection films [49,50], luminescence [51,52], solar energy conversion [53], etc. Zinc oxides are also used in care products like sunscreen and cosmetics, as they can strongly absorb UV light [54,55].

Additionally, the properties of metals can be enhanced in combination with another metal i.e., transition metal. The combination of metal oxides as nanocomposite, hence, increase interactions and effectiveness [56]. Various methods have been reported for the synthesis of nanocomposites, such as the sol-gel method [57,58], chemical vapor deposition (CVD) [59], hydrothermal methods [60], and the solid state method [61]. Among all preparation methods, co-precipitation is the easiest and most cost-effective method, and no special or complicated material and equipment is required [62].

In this work, the reduction of 4-nitrophenol using aqueous NaOH as a reducing agent in the presence of an La_2ZnO_4 catalyst could be a substitute for conservative reduction processes. Up till now, no work has done on the direct combination of Lanthanum and Zinc metals in the form of a combined oxide. Thus, in the present work, we report the synthesis of Lanthanum Zinc oxide nanocomposite La_2ZnO_4 through a simple co-precipitation method, keeping in mind the properties of Lanthanum and Zinc. The prepared nanocomposite was characterized by many useful techniques, i.e., FTIR Fourier transform infrared spectroscopy, ultraviolet spectroscopy, XRD X-ray diffraction, SEM scanning electron microscopy, and PL photoluminescence. Herein, 4-nitrophenol was reduced to 4-aminophenol in the presence of the La_2ZnO_4 composite applying aq. NaOH as a reducing agent. This scheme did not involve a specific solvent and was established at room temperature. Hence, the current method offers an eco-friendly route for the catalytic hydrogenation of 4-nitrophenol to 4-aminophenol.

2. Materials and Methods

2.1. Materials

Lanthanum nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) (99.99% pure), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (99% pure), sodium hydroxide anhydrous pellets (NaOH) (98% pure), and methanol (CH_3OH) (99.8%) were purchased from Sigma Aldrich and used as received without any further purification treatment. All chemicals, including deionized water (DI) used during the experiment, were of analytical reagent grade.

2.2. Synthesis of La_2ZnO_4

The process of synthesizing the La_2ZnO_4 nanocomposite, was followed according to the work reported by Tinwala et al. [63]. The La_2ZnO_4 nanocomposite was synthesized via the co-precipitation method, using the precursors lanthanum nitrate $\text{La}(\text{NO}_3)_3$, zinc nitrate $\text{Zn}(\text{NO}_3)_2$, deionized water, and methanol as starting materials. Sodium hydroxide NaOH was used as a precipitating agent. The solutions of $\text{La}(\text{NO}_3)_3$ and $\text{Zn}(\text{NO}_3)_2$ 150 mL each were prepared separately by dissolving them in the solvent. The concentration of mixtures prepared was 0.1 M for the Lanthanum nitrate solution and 0.003 M for the Zinc nitrate solution. 0.2 M concentrated solution of the precipitating agent was also prepared.

Co-precipitation was done by combining both the mixtures and titrating by adding the precipitating agent i.e., NaOH dropwise, while stirring at 200 rpm with a magnetic stirrer and heating at 70 °C temperature for 6 hrs. Initially the pH was ~4, and the precipitating agent was added until the pH reached ~11. On completion of the precipitation, the solution was filtered using Whatman filter paper and washed with acetone several times in order to remove all the byproducts. The as-prepared material was dried in an ordinary oven at 80 °C for 24 h, and then ground using a mortar and pestle. The dried powder was calcined at 400–450 °C for 4 h.

2.3. Characterization

The Lanthanum-based Zinc oxide nanocomposite was characterized with different analytical techniques. Crystalline size and structure were determined by X-ray diffraction on (JDX-3532, JEOL, Tokyo, Japan), X-Ray Diffractometer, using $\text{Cu-K}\alpha$ ($\lambda = 1.5046 \text{ \AA}$) radiation at a tube voltage of 40 KV and 20 mA current. The morphology was found by using scanning electron microscopy SEM (JSM-5910, JEOL, Tokyo, Japan); a band gap was found via ultraviolet spectroscopy UV. Photoluminescence spectroscopy PL was also used to check the optical properties of the prepared sample as a semiconductor. Fourier transform infrared spectroscopy FTIR (IR Prestige 21, Shimadzu, Kyoto, Japan) was used to identify the presence of any unwanted substance in the sample after calcination.

2.4. Catalysis for *p*-Nitrophenol Conversion

In a typical test, to 20 mL of a 0.1 $\text{mmol}\cdot\text{L}^{-1}$ aqueous solution of *p*-nitrophenol taken in a beaker, a freshly prepared aqueous solution of NaOH in distilled water was introduced. To the mixture, 0.1 g of the La_2ZnO_4 oxide was added and stirred at room temperature. The disappearance of the yellow color of *p*-nitrophenol was monitored by UV-VIS spectroscopy (Tensor II BRUKER, Billerica, MA, USA).

3. Results and Discussion

3.1. X-ray Diffraction

The morphological and structural analysis of the as-developed catalyst material was carried out by various physicochemical characterizations. The crystallographic and structural confirmation of the La_2ZnO_4 nanocomposite was done by means of powder X-ray diffraction analysis. The XRD pattern of the La_2ZnO_4 nanocomposite treated at 400–450 °C is shown in Figure 1 with 2θ range from 20° to 60° at room temperature. A mixed phase of La_2O_3 and ZnO is formed, which is evident from the graph. All the diffraction peaks refer to hexagonal phase La_2ZnO_4 and are in good agreement with the standards (ICCD card No. 00-002-0688) for lanthanum oxide phase and (ICCD card No. 00-001-1136) for zinc

oxide phase, respectively. In Figure 1, the peaks at 22° (100), 26° (002), 44° (101), and 46° (103) correspond to La and peaks at 36° (002) and 57° (110) match up with the multiple similar reported XRD patterns. Besides, the peaks at 31° (101) and 36° (100) appeared due to the synergistic impact of La/Zn oxides, as both of these oxides give peaks around such 2 theta positions, singly. Moreover, few additional peaks are observed in the XRD pattern i.e., 40° (101), 42.3° (100), 51° (101), and 55° (111), which is indication of the successful formation of the mixed metal oxide composite [64–66].

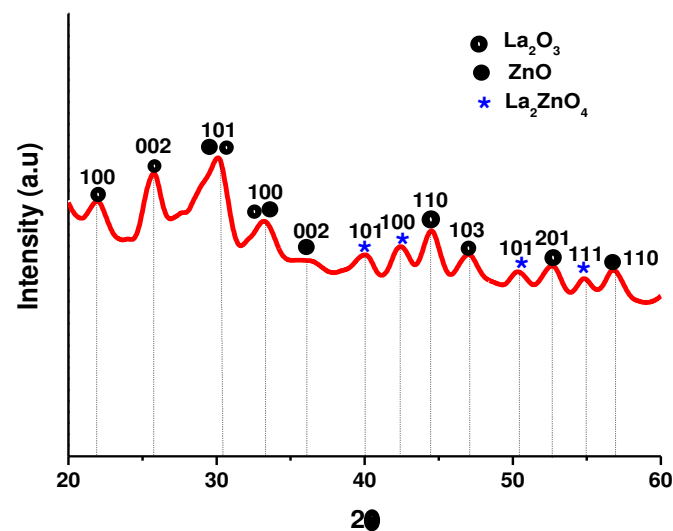


Figure 1. X-ray diffraction spectrum of La_2ZnO_4 .

The crystallite size of the sample calcined at 400 °C was calculated by using Debye-Scherrer's equation [67], which is given below:

$$D_{hkl} = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where D_{hkl} is the average crystalline size perpendicular to the crystal phase (hkl) K is constant, λ is 1.5406 Å, and β is full width half maxima of the peak at (100) plane (Figure 1) [67]. The average crystallite size of the nanocomposite calculated using the above equation is 8.62 nm for the sample calcined at 400–450 °C.

3.2. Scanning Electron Microscopy

The morphological analysis was done with scanning electron microscopy (SEM, Hitachi High-Tech, Seoul, Korea). Figure 2 represents the hexagonal morphology of the nanocomposite prepared La_2ZnO_4 via scanning electron microscopy (SEM). At some places, aggregates of the nanocomposite were observed due to the presence of binary oxides of lanthanum and zinc. It is clearly seen that the composite is in crystalline form and four pictures shows the presence of Zn particles on the surface of Lanthanum crystals, forming a unique nanocomposite.

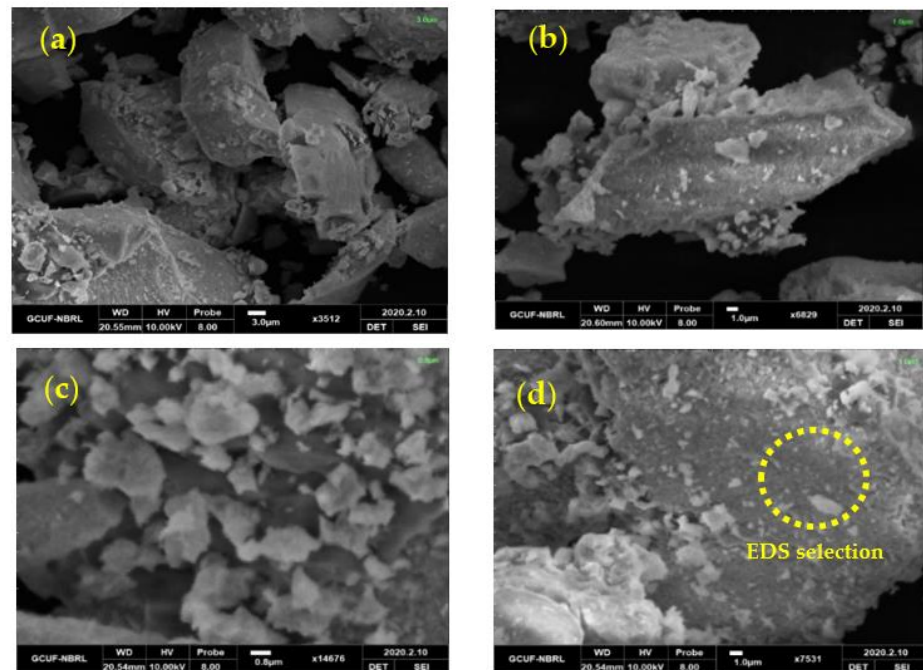


Figure 2. Scanning electron microscopy images of the La_2ZnO_4 nanocomposite at different resolutions (a) at 3.0 μm (b) 1.0 μm (c) 0.8 μm (d) Selection of EDX on SEM Pattern.

3.3. Energy Dispersive Spectroscopy

Elemental composition and purity of the as-synthesized La_2ZnO_4 composite was determined by EDS analysis (MIRA3 TESCAN, Brno, Czech Republic), as presented in Figure 3. Uniform distribution of Zn, La, and O throughout the whole matrix is evident from the EDS spectrum and mapping. No other peak corresponding to any impurity was observed. It is witnessed that the composite contained a smooth surface, which could be associated with the homogenous mixing of Zn and La oxides in the composite, resulting in a single phase surface morphology.

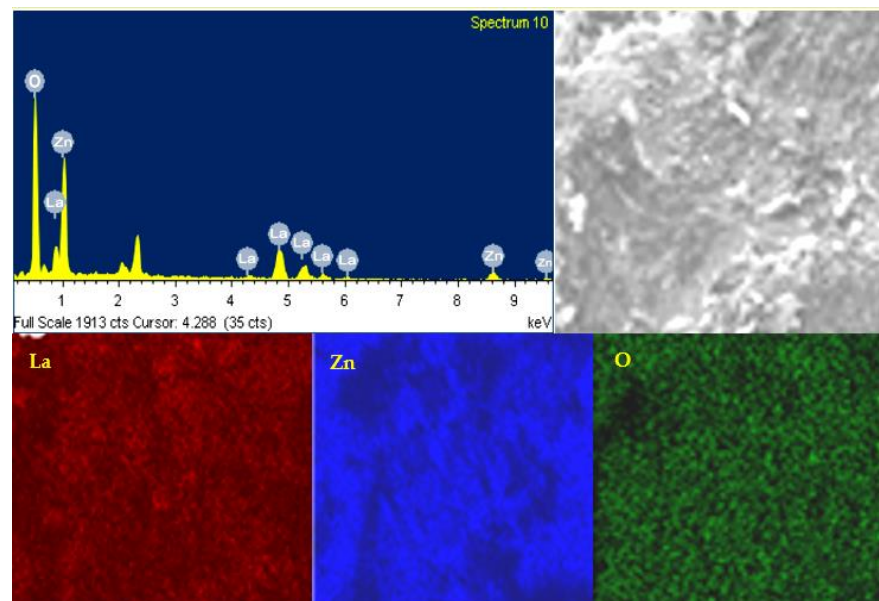


Figure 3. EDS spectrum and mapping for the La_2ZnO_4 nanocomposite.

3.4. FTIR Analysis

Figure 4 shows the FTIR spectrum of the La_2ZnO_4 nanocomposite. The characteristic peaks at 529.37 and 831 cm^{-1} clearly indicate the presence of Zn–O stretching vibration and peaks at 717.98 – 591.70 cm^{-1} confirms the presence of ZnO and La [68]. Slight shifting of peaks is noticed due to the formation of the nanocomposite. The peak at 3434.85 cm^{-1} represents the La_2O_3 stretching vibration. A peak with very weak intensity at 854.24 cm^{-1} can be assigned to the residual nitrate ion. Other characteristic absorption bands from 2359.95 to 1458.21 cm^{-1} may be due to the presence of water molecule, C=C, stretching of C–H and C–C, respectively. The difference in peak positions of the starting lanthanum nitrate and the as-synthesized composite can be witnessed in the reported FTIR spectrum [69]. The appearance of new peaks at 649 , 1393 , and 2361 cm^{-1} and the disappearance of specific nitrate peaks indicate the formation of the La oxide composite [70].

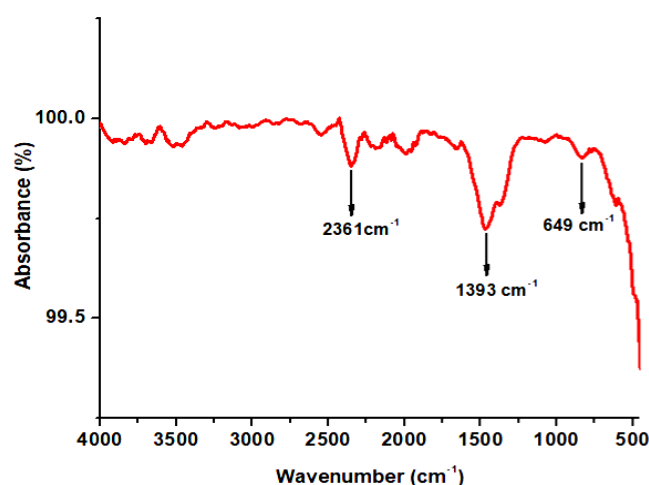


Figure 4. FTIR spectra of the La_2ZnO_4 nanocomposite.

3.5. UV-Visible Spectroscopy

Optical properties of nanocomposite La_2ZnO_4 were investigated by UV-Vis absorption spectra using a UV-Visible spectrophotometer (PharmaSpec UV-1700, Shimadzu, Kyoto, Japan), as shown in Figure 5a. It was noted that band-edge absorption of the synthesized La_2ZnO_4 is located in the near UV region. The optical band gap was calculated by using the following equation [71], as shown in Figure 5b:

$$\alpha = A(h\nu - E_g)^n / h\nu \quad (2)$$

where A and n is a constant, equal to $\frac{1}{2}$ for the direct band gap semiconductor. The spectra identify UV active optical properties of the nanocomposite. It was noted that due to very low concentrations of Zinc, as compared to Lanthanum, the band gap had minute changes, although both metals are good semiconductors; however, for better efficiency, the concentration of Zn metal could be increased. The prepared composite could be applied as a UV light photocatalyst.

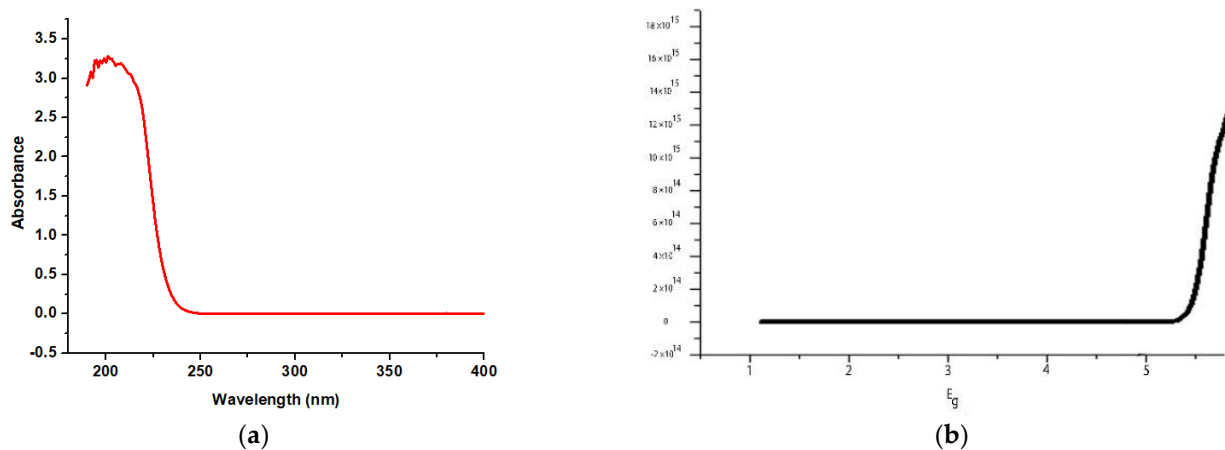


Figure 5. (a) Absorption spectra (UV-Vis) of the La_2ZnO_4 nanocomposite (b) Tauc plots of $(\alpha h\nu)^2$ versus $h\nu$ of the La_2ZnO_4 nanocomposite.

3.6. Photoluminescence Observation

The PL spectra of the La_2ZnO_4 nanocomposite is shown in Figure 6. Small variations in the absorption peaks, due to the formation of nanocomposites, were noticed. The position of emission bands becoming less intense may be due to the strain in crystal lattice to accommodate larger Lanthanum atoms with Zinc metal as oxide. If the UV spectrum of the as-proposed composite is compared with pure lanthanum nitrate, a blue shift is observed, a result of the addition of zinc, attributed to wider band gap of ZnO [72]. The results suggest that the as-synthesized nanoparticles can absorb radiation in UV and in the visible region, as well from solar light, indicating that the La_2ZnO_4 composite could be useful as a visible light photocatalyst.

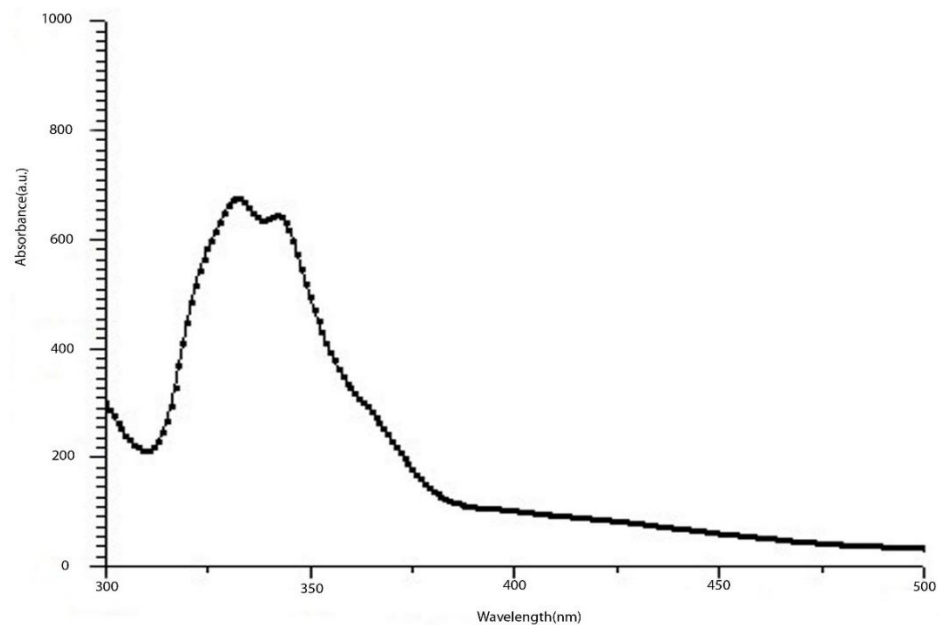


Figure 6. PL spectra of the La_2ZnO_4 nanocomposite.

3.7. Catalysis Process

The catalytic performance for hydrogenation reaction was examined by the catalytic reduction of 4-nitrophenol into 4-aminophenol, shown in Figure 7. Before the explanation of results of 4-NP reduction, the common mechanism and logical reasons for the enhanced

hydrogenation reactions performance can be ascribed due to the presence of mixed-phase binary oxides nanoparticles in nanocomposite form. The reduction capability of the catalyst material depends on the mutual electron transfer process within the composite system. In the case of the present catalyst, La_2ZnO_4 exhibits a higher catalytic performance, resulting from both the constituent elements. The brief mechanism could be explained as follows; in La_2ZnO_4 , the La_2O_3 and ZnO sites exhibited selectivity in initiating the reduction reactions at the mixed-phase binary oxide of the La_2ZnO_4 interfaces; further, this composite improved the electron transfer phenomenon as well boosted the reaction synergistically. These collective factors enhanced the overall catalytic performance of the nanocomposite material.

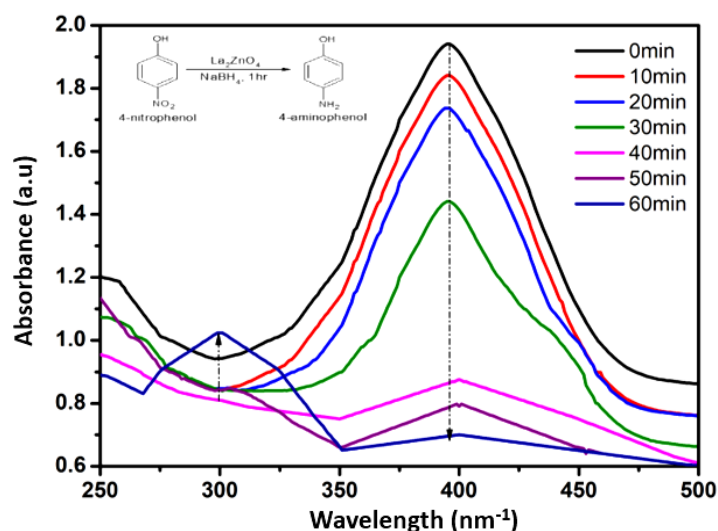


Figure 7. Photocatalytic reduction of 4-nitrophenol into 4-aminophenol.

It was observed that the conversion of 4-nitrophenol to 4-aminophenol with NaOH as a reducing agent in the presence of La_2ZnO_4 reducing catalysts took 60 min (when the color of the mixture changed from yellow to colorless). Comparatively, this decolorization requires 5.5 h with NaOH , in the absence of a catalyst. The appearance of a new peak at 300 nm^{-1} corresponds to the absorbance by 4-aminophenol and is an indication of successful conversion [73,74]. The observed UV-visible absorbance peaks of the reactants and the product are significantly isolated at $\sim 400 \text{ nm}$ and $\sim 300 \text{ nm}$, respectively. Furthermore, the concentrations of 4-nitrophenol were estimated from absorbance at $\sim 400 \text{ nm}$ using the respective calibration curve. Therefore, it can be deduced that the mild reducing ability of NaOH could be efficiently enhanced with the addition of the La_2ZnO_4 composite.

3.8. Kinetics of the Reduction Catalysis

The kinetic mechanism of 4-nitrophenol reduction with NaOH was studied with the La_2ZnO_4 catalyst. It typically follows the pseudo-first-order reaction owing to the concentration of 4-nitrophenol. The equation for the pseudo-first-order reaction is given in Equation (3) [75]:

$$\ln(C_t/C_0) = \ln(A_t/A_0) = -kt \quad (3)$$

Here C_t and C_0 represent the concentrations of 4-nitrophenol at time t and $t = 0$, respectively. A_t and A_0 corresponds to the absorbance of 4-nitrophenol at time t and $t = 0$ respectively, at peak position of 400 nm^{-1} . k is the rate constant of the reaction.

Moreover, when natural log of concentration/absorbance was plotted as a function of time, a significant decrease can be witnessed (Figure 8). The slope of the graph gave the rate constant of the reaction, which is found out to be $k = 0.012 \text{ min}^{-1}$.

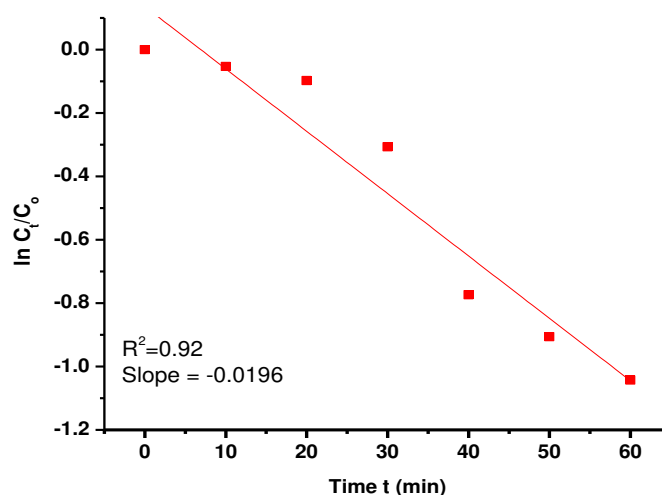


Figure 8. The kinetic plot for the adsorption-catalytic reduction of 4-nitrophenol.

4. Conclusions

Lanthanum-based Zinc oxide nanocomposites were synthesized by co-precipitation method using water as a solvent. The reaction between both the precursors in the presence of water produces hydroxyl ions for precipitation. The hexagonal crystalline structure with crystallite size of 8.62 nm was observed after calcination at 450 °C, detected by XRD. The morphology was confirmed by SEM; all the images show the presence of Zinc on the surface of Lanthanum, hence forming the La₂ZnO₄ nanocomposite. No evidence of the presence of separate La and Zn was found. The PI spectra indicated that the band gap of La metal can be reduced by the addition of Zn metal, if an efficient amount is used. The nanocomposite prepared was found to have strong photocatalytic efficiency. Co-precipitation, the method that was adopted for synthesis, was cost-effective and simple, as compared to other reported methods. In addition, the as-developed nanocomposite material showed enhanced catalytic performance for complete reduction of 4-nitrophenol into 4-aminophenol within 60 min. The enhanced 4-NP reduction may be ascribed to the synergistic effects of binary oxides sites of the La₂ZnO₄ nanocomposite. The findings herein could pave the way for the fruitful study and development of heterogeneous catalysts for eco-friendly environmental applications.

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