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Hydrothermal Synthesis of Zinc Cobaltite ($ZnCo_2O_4$) Nano Particles for Green Hydrogen Production via Water Splitting by Photocatalysis

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Abstract
Zinc cobaltite (ZnCo2O4) nano particles have been synthesized by hydrothermal method for hydrogen generation by photo catalytic water splitting reactions. To indicate the nano-catalyst's structure, the samples' characterization has been implemented using XRD, FTIR, SEM and TEM analysis. The characterization revealed successful synthesis of the ZnCo2O4 nano particles. UV–Vis/DRS examination shows that the ZnCo2O4 nanoparticles, especially (Zn: Co) oxide= (1:1.25) sample exhibited superior visible light capture compared to other samples. The photo catalytic activity of photo catalysts were tested for photocatalytic hydrogen generation. The best rate of hydrogen yield of 19ml H2/g. catalyst/min was produced by the optimum ratio of ZnCo2O4 nano-catalysts, (Zn: Co) oxide= (1:1.25). The nano-catalysts' photocatalytic activity has been slightly diminished by repeated usage, which is an evidence of the catalyst's stability. The reaction temperature effect on the rate constant revealed an apparent activation energy for ZnCo2O4 nanoparticles, (Zn: Co) oxide = (1:1.25) of 14 kJ. mol-1. This is the activation energy needed for the photocatalytic reaction's slowest step. In addition, the effect of scavenger concentration on photo catalytic water splitting reactions for hydrogen production also checked.

Keywords**:** Hydrogen production, Water Splitting, ZnCo2O4 Nano Particles, Photo catalysis.

1. Introduction

The present level of worldwide energy consumption necessitates the identification and utilization of optimal alternative energy sources. Particularly, there is a need for sustainable and renewable energy processes that are environmentally benign, as they produce no carbon emissions in contrast to fossil fuels [1]. Hydrogen is widely acknowledged as a highly promising and environmentally sustainable energy source, thus positioning it as a potential transitional solution for the substitution of fossil fuels [2]. Water vapour is produced during the combustion of H2, and its calorific value (141.9 kJ/g) is three times that of gasoline (47 kJ/g) and 2.6 times that of natural gas (54 kJ/g). Hydrogen has a lower density and molar mass at STP (0.08988 g/L and 1.008 g/mole, respectively) than other fuels like ethanol and natural gas. [3]. In recent times, there has been a significant focus on the exploration of various techniques for hydrogen production, as it is widely regarded as a highly suitable renewable energy source. The water splitting method is currently receiving significant attention from researchers as the most promising approach for hydrogen production, among various other methods available [4]. Solar energy is the best, cleanest, and most renewable source of energy. It can be used to split water molecules into molecular hydrogen, which is a clean fuel with a 120 MJ/kg energy density [5]. Subsequently, photocatalytic water splitting attracted a lot of attention due to its potential. In the last 40 years, scientists have experimented a wide range of photocatalyst materials and systems by using UV and visible light to catalyse the splitting of water. Photocatalytic water splitting could be classified as either photochemical or photoelectrochemical (PEC). Multiple research reviews concluded that the high capital cost of PEC devices precludes their use in solar hydrogen production. One-step photochemical water-splitting systems will be the primary focus of this article [6]. The photo catalytic water dissociation reaction, which is responsible for the production of a stoichiometric amount of H2 and O2, occurs when photons are absorbed by a photo catalytic material that possesses a band gap energy that is compatible with the incident irradiation. Improved interfacial charge separation and a large surface area providing enough active sites which are responsible

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for the enhanced activity of photo catalytic nano-materials compared to their bulk counterparts [7]. Nano photo catalysts' efficiency rates can be improved by combining them with sensitizers, co-catalysts, or scavengers, as well as by adjusting their particle size, chemical composition, microstructure, crystalline phase, morphology, surface modification, band gap, and flat band potential [8]. Fujishima and Honda discovered TiO2 as the first photocatalyst for hydrogen production from water in 1972, continuous efforts have been made to design inorganic and organic semiconducting materials like metal oxides, metal nitrides, carbon nitrides, metal organic frameworks, covalent organic frameworks, etc. for efficient photocatalytic hydrogen evolution. However, photocatalytically efficient materials are still needed for practical applications [5]. The metal oxides in question should have high electrical conductivity, be readily available, and be thermally and chemically inert [9]. To date, various single metal oxides such as CuO, ZnO, NiO, and Co3O4 have been extensively investigated as photocatalytic materials with functional properties. Nevertheless, the photocatalytic applications of single metal oxides are significantly restricted due to their low electrical conductivity and inadequate stability. Because of this, a cobalt-containing transition bimetallic oxide with a spinel structure (MCoO; M = Zn, Ni, Mn, and Fe) was progressed, and the synergistic impact between several metal ions can increase not only its electrical conductivity, but also its active sites and stability. One such material is a typical p-type semiconductor, ZnCo2O4 (ZCO) which strongly absorbs both ultraviolet (UV) and visible light. To further enhance its photo catalytic performance, ZCO's spinel structure contains Co3+/Co2+, forming a redox pair that gives the material higher conductivity and more redox sites than single metal oxides [10]. The current research aims to synthesis ZnCo2O4 (ZCO) nano particles using hydrothermal method by altering the mass concentration of the cobalt content, Zn: Co = (0.25, 0.50, 0.75, 1 and 1.25 gm) under the same conditions, as well as its characterization and use in the field of photocatalysis with the purpose of enhancing the efficiency of the water splitting process and hydrogen production. The degree of doping, the influence of scavenger concentration, the influence of temperature, and the stability of the photocatalyst are the parameters that were being investigated. A discussion has also taken place of the kinetic analysis of the photocatalytic water splitting process.

2. Materials and Methods

2.1. Materials

Cobalt nitrate ($Co(NO_3)2.6\ H_2O$) and zinc nitrate($Zn(NO_3)2.6\ H_2O$) were purchased from (Fisher scientific UK, Loughborough, England) and (Loba Chemie Pvt.Ltd company, Mumbai,India) respectively. Ammonium hydroxide (NH_4OH,35% NH3) was purchased from (EL Pharaohs company ,Cairo, Egypt).Sodium sulphite (Na_2SO_3) and sodium sulphide (Na2S) , used as chemical reagents , were purchased from (Alpha Chemika company, India). Distilled water was used throughout experiments.

2.2. Synthesis of photo catalyst

2.2.1 Synthesis of zinc cobaltite ($ZnCo_2O_4$) nano particles via hydrothermal method

Hydrothermal synthesis was conducted to prepare five samples of $ZnCo_2O_4$ nano-catalysts with different mass concentrations of the cobalt content, Zn : Co = (0.25, 0.50, 0.75, 1 and 1.25 gm). Different amounts of cobalt nitrate ($Co(NO_3)2.6$ H2O) were mixed with a fixed amount of zinc nitrate($Zn(NO_3)2.6\ H_2O$) according to the previous ratios and added to 40 mL of distilled water by continuous magnetic stirring at ambient temperature for a duration of 30 minutes to ensure the uniform distribution of each component. The solution was subjected to dropwise addition of liquid ammonia to adjust the pH of the solution to be around 10. Following this, the solution that had been prepared was poured into a Teflon-lined stainless-steel autoclave with a volume of 70 mL. The autoclave was held at a temperature of 120°C for 6 hours. The obtained precipitates were collected through centrifugation at a speed of 5000 rpm and subsequently subjected to multiple washes using distilled water. The precipitates were dried at a temperature of 60℃ for 20 hours. The brown black color of the resultant nano powder indicates the development of $ZnCo_2O_4$ nano particles [11]. And its volume changes with time [12].

2.2.2 Characterization.

The phase existence and degree of crystallinity of the ZnCo2O4 nanoparticles were identified by X-ray Powder Diffraction-XRD-D2 Phaser (30 kV, 10 mA, Cu-K radiation with λ=1.54184 A∘; Bruker Corporation, Germany). A scanning electron microscope (SEM, Model JSM -IT200 LA; JEOL Ltd., Tokyo, Japan) operating at 20 kV was used to study the morphology and a high resolution image of nano-catalyst was taken using a transmission electron microscope (TEM, Model JTM-1400 plus; JEOL Ltd., Tokyo, Japan) for size determination. The FT-IR study was investigated using a Bruker Tensor 37 FT-IR spectrometer to indicate the functional groups of the synthesized nano-catalyst. An essential characterization tool for choosing a specific application is optical analysis, the energy needed to shift the electrons from the valence band to the conduction band was calculated using it. Thus, an Ultraviolet Visible Diffused Reflectance spectrometer (UV-vis-DRS) (GBC cintra 3030, GBC

Scientific Equipment Pty Ltd, Australia) with a scan speed of 1000 nm/min was used to determine the optical characteristics of the prepared materials. The spectra were captured with a resolution of 2 nm over the wavelength range of 190-900 nm.

2.2.3. Green hydrogen production from water splitting by photocatalysis A photo catalytic water splitting reaction was implemented using 250 ml conical flask with a side opening and a stopper. The experiment was implemented by adding 50 mg of the nano- catalyst to an aqueous solution of scavenger compounds with a concentration of 0.5M (100 ml water: 3.9g Na2S, 6.3g Na_2SO_3). The sample was stirred by magnetic stirrer to reduce the hydrodynamic boundary layer thickness surrounding each nano -catalyst particle. The experiment was carried out using a 2000 W Halogen lamp. The O2/H2 gases pass through the opening and gather in an upside-down graduated cylinder above the water. Calculating the volume of accumulated hydrogen requires recording the rate of water

3. Results and Discussion

3.1. Scanning electron microscopy and Transmission electron microscopy (SEM) & (TEM)

The morphology study of $ZnCo_2O_4$ nanoparticles was illustrated using SEM micrograph. Fig. 1(a &b) shows the SEM images of optimum ratio of $ZnCo_2O_4$ nano-catalysts, (Zn:Co) oxide=(1:1.25). It is obvious that the nanoparticles are cubic crystal structure which agreed with the SEM analysis images [13, 14, 15]. The SEM image shows a large number of small irregular cubic structures, each lower than 100 nm in size. TEM images of the optimum ratio of $ZnCo_2O_4$ nano-catalysts, (Zn:Co) oxide=(1:1.25) was captured as shown in fig.1(c &d) to investigate that $ZnCo_2O_4$ nanoparticles with the size of 15.8-36.7 nm. The presence of faceted nanoparticles with a pockmarked structure was clearly identified which agreed with the TEM analysis images [13,14]. It is confirmed that the synthesized $ZnCo_2O_4$ nanocatalysts were successfully prepared with nano size range.

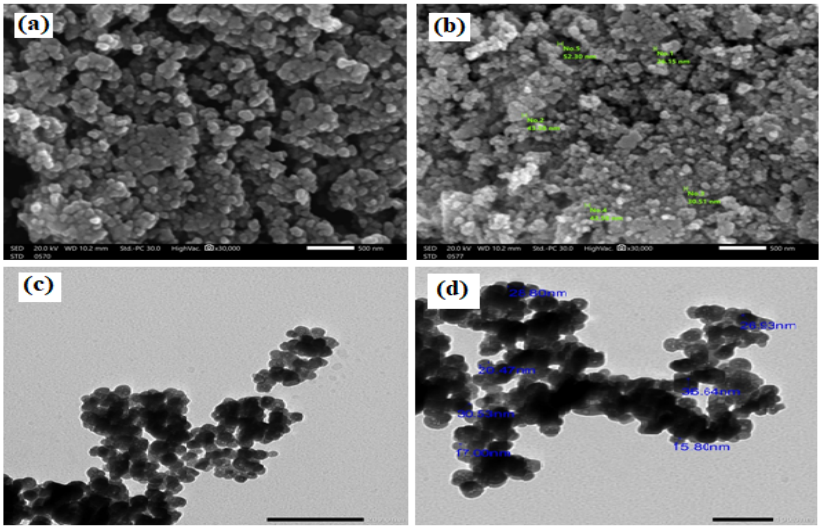

Figure 1. (a, b) SEM images and (c,d) TEM images of the optimum ratio of synthesized $ZnCo_2O_4$ nano-catalysts, (Zn: Co) oxide=(1:1.25).

3.2 X-Ray Diffraction (XRD)

Figure 2 demonstrates the X-ray diffraction patterns of the prepared $ZnCo_2O_4$ nanoparticles. The XRD pattern of the sample displays the reflections with hkl values of (111), (220), (311), (222), (422), (511), (440), (531), (620) and (533) and the planes obviously confirm the corresponding 2θ values at 18.99°, 31.236°, 36.806°, 38.505°, 55.590°, 59.287°, 65.157°, 68.545°, 74.076° and 78.358°and which confirms that the prepared $ZnCo_2O_4$ nanoparticles are spinel with cubic phase with space group Fd-3m(227). The obtained XRD peaks are in good agreement with JCPDS card no # 23-1390 which indicates cubic phase with no impurities [16 , 17 , 18 ,19 , 20, 21]. Bragg's Law equation is used to calculate the inter-planar separation (d-spacing) between atoms [2]:

$$D = 0.9\lambda\ \beta\cos\theta \qquad (1)$$

$2d\sin\theta = n\lambda$ (2)

where λ is the wavelength of the X-ray beam (0.154184 nm), β is the FWHM (radian), θ is the diffraction angle (degree), d is the interplanner spacing (nm), and D is the particle diameter (nm). Therefore, the inter-planar spacing between atoms (d-spacing) were found to be 0.519 , 0.317, 0.27, 0.259, 0.182,0.172, 0.157 ,0.15 , 0.14 and 0.134 at 2θ18.99°, 31.236°, 36.806°, 38.505°, 55.590°, 59.287°, 65.157°, 68.545°, 74.076° and 78.358° respectively. Hence, it can be concluded from the XRD data the successful synthesis of $ZnCo_2O_4$ nanoparticles.

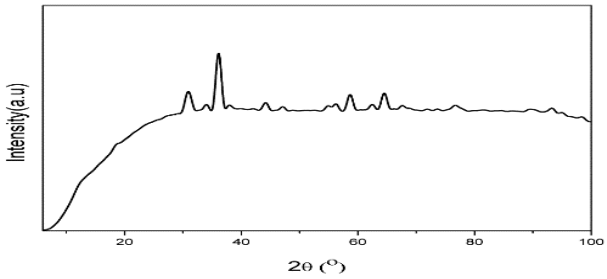

Figure 2. X-ray diffraction analysis of the synthesized optimum ratio of $ZnCo_2O_4$ nano-catalysts, (Zn: Co) oxide=(1:1.25).

3.3. Fourier Transform Infrared (FTIR) analysis

Figure 3 shows the FT-IR spectrum of synthesized $ZnCo_2O_4$ nanoparticles for chemical information and major functional groups. The presence of water molecules is indicated by a broadband in the range of 3331 cm^{-1} attributed to O-H stretching and a peak at 1631 cm^{-1} for the bending vibration mode of the H-O-H group. The metal-oxygen bond of Co-O and Zn-O stretching vibrational modes are responsible for the formation of the $ZnCo_2O_4$ spinel structure, as are the strong and sharp peaks at 572 and 665 cm^{-1}. Peak values close to which found [13, 16, 17,22] indicating the successful synthesis of $ZnCo_2O_4$ nanoparticles.

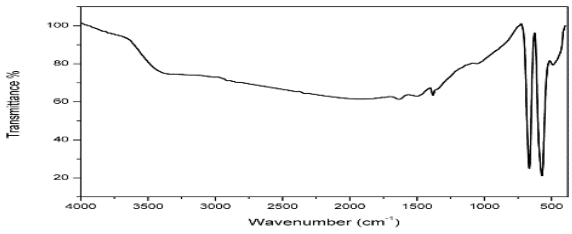

Figure 3. FT-IR spectrum of optimum ratio of the synthesized $ZnCo_2O_4$ nano-catalysts, (Zn: Co) oxide=(1:1.25).

3.4 UV-visible DRS analysis

The UV-Vis-DRS analysis was performed in the wavelength range of (200-900) nm and the results are showed in Fig.4. From the UV-Visible reflectance analysis, the band gap energy of the manufactured $ZnCo_2O_4$ nano-catalyst was determined from Tauc plot as shown in fig.4 where $F(R) = \frac{(1-R)^2}{}$ [17,23]. So, the band gap energy of the optimum ratio of $ZnCo_2O_4$ nano-catalysts, (Zn: Co) oxide = (1:1.25) sample was found to be 1.9 eV at wavelength= 652 nm. As a result, the optimum ratio of $ZnCo_2O_4$ nano-catalysts, (Zn: Co) oxide=(1:1.25) would be active in the visible region, which is a good indication for the successfully synthesis of $ZnCo_2O_4$ nanoparticles with optimal band gap width required for photocatalytic reaction for hydrogen production in the visible region.

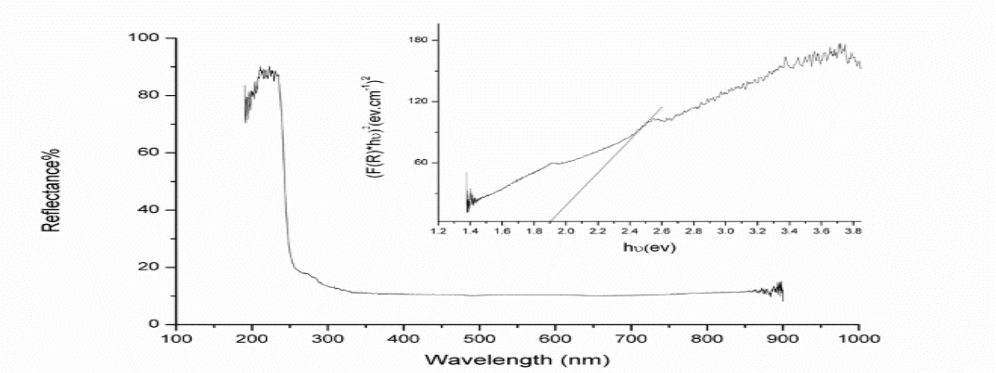

Figure 4. DRS analysis for solid and Tauc plot for band gab determination for optimum ratio of $ZnCo_2O_4$ nano-catalysts, (Zn: Co) oxide = (1:1.25).

3.5- Application of zinc cobaltite ($ZnCo_2O_4$) nanoparticles in photo catalytic hydrogen production

The prepared zinc cobaltite ($ZnCo_2O_4$) Nps samples were investigated for H_2 evolution under visible light irradiation of a 2000 watt halogen lamp. Hydrogen yield was affected by changing some parameters as the cobalt source doping percentage, temperature, the scarifying agents' concentration and its stability.

3.5.1 Effect of cobalt concentration with $ZnCo_2O_4$ nanoparticles

Figure 5 (a) demonstrates the volume of hydrogen generated as a function of time for prepared zinc cobaltite ($ZnCo_2O_4$) Nps samples with different ratios of cobalt content , Zn : Co = (1: 0.25, 0.50, 0.75, 1 and 1.25 gm) under the same conditions. It is obvious that increasing cobalt content results in an increase in the rate of hydrogen production. The anticipated increase can be attributed to the presence of Co^{3+}/Co^{2+} in the spinel structure ZCO, which forms a redox pair. This redox pair enhances conductivity and increases the availability of redox sites compared to single metal oxides, thereby enhancing the photo catalytic performance [10]. So, the ratio of (Zn: Co) oxide = (1:1.25) prepared by the hydrothermal method produced the highest evolution rate of 19 ml H_2/g.catalyst/min as demonstrated in Figure 5.

3.5.2 Sacrifying agents' concentration

In major techniques, water splitting to produce hydrogen gas requires sacrificial reagents to catch photocatalyst holes and boosts hydrogen generation photo-efficiency. Sulfite ions can change the photo-efficiency of hydrogen creation and react with an intermediate product, even without the presence of a photo catalyst. Understanding the role of Na_2S-Na_2SO_3 in photocatalytic hydrogen production is very critical [2]. Figure 5 (b) displays the rate of photo catalytic H_2 generation of optimum ratio of prepared $ZnCo_2O_4$ nano-catalysts, (Zn:Co)oxide=(1:1.25) sample at different Na_2SO_3/ Na_2S scavenger concentrations. By comparison ,the hydrogen yield for a Na_2SO_3/ Na_2S concentration of 0.5/0.5 M was the highest for the tested concentrations .The rate of hydrogen generation for a concentration of 0.75/0.75 M was higher than that for a concentration of 0.25/0.25 M. So,0.5/0.5 M is the optimum ratio used with $ZnCo_2O_4$Nps, (Zn:Co) oxide=(1:1.25) sample prepared by the hydrothermal method for water splitting hydrogen production.

3.5.3 Stability of $ZnCo_2O_4$ nanoparticles

The nano-catalyst's stability is critical for its application. Accordingly, the stability of the $ZnCo_2O_4$ nano particles was tested using 2000 W Hg-lamp for five consecutive. Fig.5 (c) shows the hydrogen production vs. time for the optimum ratio of ($ZnCo_2O_4$) nano-catalysts, (Zn: Co) oxide=(1:1.25) sample using a halogen lamp for five consecutive cycles. It is important to note that after reusing, the hydrogen production efficiency of the photolyzed water has been slightly affected. The hydrogen yield wasn't changed till cycle three then slightly decreased till the fifth cycle. This might be because of blocking of some active sites of the catalyst surface due to oxidation reaction. The results confirms that prepared $ZnCo_2O_4$ Nps, (Zn:Co)oxide=(1:1.25) sample maintained active for photo catalytic hydrogen production, indicating that the sample had sustained stability.

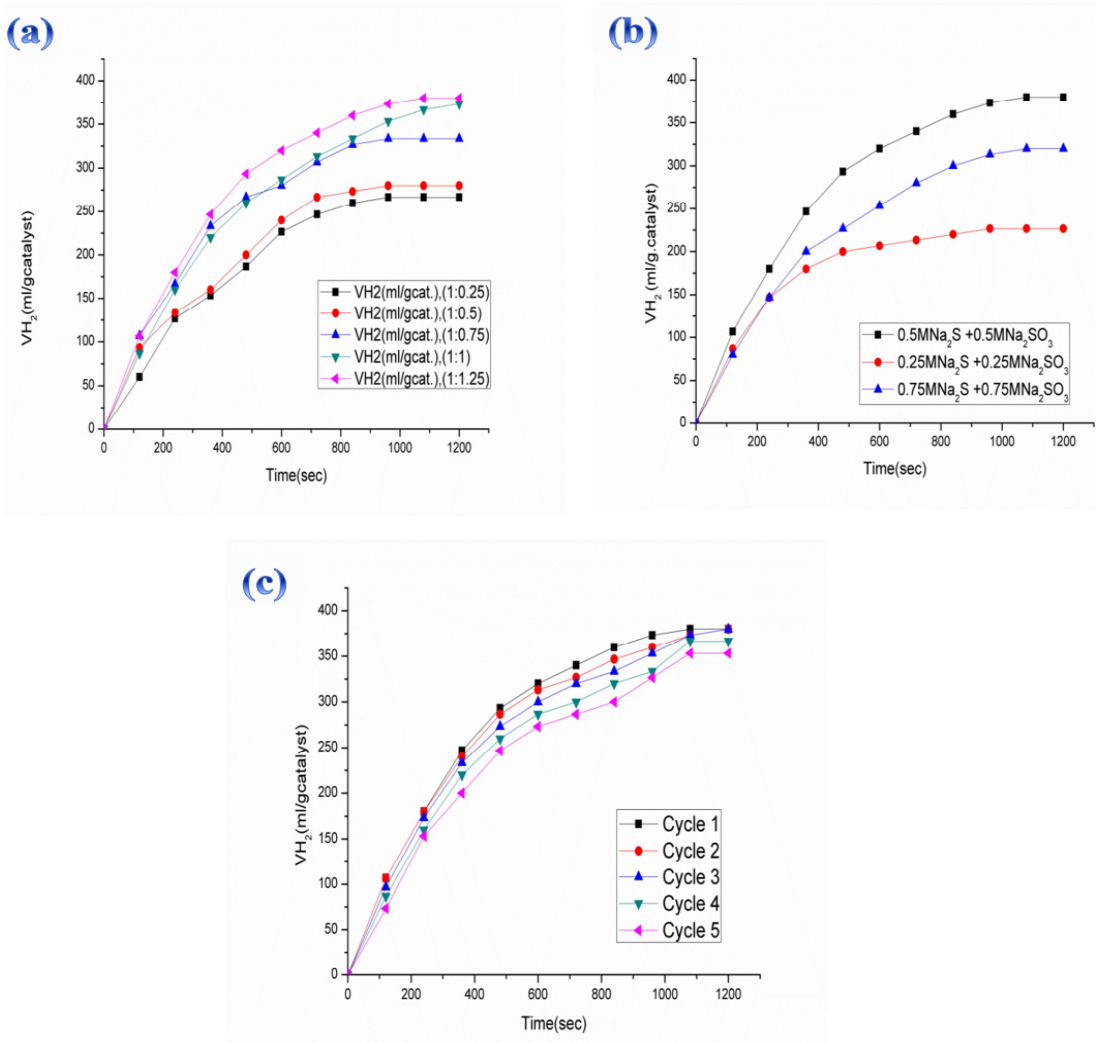

Figure 5. The hydrogen specific evolution as a function of time for: (a) $ZnCo_2O_4$ (ZCO) nano-catalysts by altering the mass concentration of the cobalt content (i.e. 0.25, 0.50, 0.75, 1and 1.25 gm also) with a fixed amount of zinc content(1 gm), (b) Photocatalytic H_2 production rates over the optimum ratio of synthesized $ZnCo_2O_4$ nano-catalysts, (Zn: Co) oxide=(1:1.25) at different concentration of Na_2S /Na_2SO_3 scavenger. Conditions: 50 mg of catalysts, 100 ml of solution, 400 rpm, 2000 W Hg-lamp. (c) hydrogen evolution rate for 5 runs of the same $ZnCo_2O_4$ nano-catalyst, (Zn: Co) oxide=(1:1.25).

3.5.4 Effect of temperature and the kinetic study

Temperature is a measure of the kinetic energy of a system, so higher temperatures indicate more collisions per unit of time and a greater average kinetic energy of molecules. Therefore, the general consensus is that increasing the temperature of a chemical process will speed up the reaction rate. This may be the case most of the time, but when comparing nano scale structures to those at bulk scales, unexpected behaviors often exhibit [24]. Fig.6 (a) demonstrates the hydrogen specific evolution vs. time for the optimum ratio of ($ZnCo_2O_4$) nano-catalysts, (Zn:Co)oxide=(1:1.25) sample was synthesized using the hydrothermal method at various temperatures, specifically 20, 40, and 50℃. As indicated in the figure, the rate of hydrogen creation increases as the temperature raises up to 50℃. As a result, increasing the temperature causes an increase in kinetic energy, more collisions per unit time, easier transport of molecules to active zones, and a decrease in reaction time [24]. Arrhenius equation provides a quantitative framework for understanding the relationship between activation energy and the rate at which a chemical reaction occurs. The activation energy can be mathematically represented by the Arrhenius equation as follow[25]:

$$K = A\, e^{-E/RT}$$

Which leads to ,

$$\ln K = \ln A - \frac{E}{RT}$$

Where A is the frequency factor for the reaction, R is the universal gas constant, T is the temperature (in Kelvin), and k is the reaction rate coefficient where k has been calculated to be 6 $x10^{-7}$ (mole/sec) .Fig.6 (b) shows a graph of ln k vs. 1/T for the optimum ratio of ($ZnCo_2O_4$) nano-catalysts , (Zn :Co) oxide =(1:1.25) sample. The slope of the curve shows the process's perceived activation energy. So, the activation energy was found to be 14 kJ. mol^{-1} for the optimum ratio of ($ZnCo_2O_4$) nano-catalysts, (Zn :Co) oxide = (1:1.25). The apparent activation energy is indicative of the activation energy associated with the slowest step within a series of multiple steps in the reaction. Based on the findings of Hisatomi etal., it can be inferred that the apparent activation energy is predominantly influenced by processes taking place within the surface of the photocatalyst rather than the dissociation of water molecules and the subsequent formation of hydrogen and oxygen bonds [2]. Therefore, the obtained results shows ($ZnCo_2O_4$) nano-catalyst surface is more active than that of RGO/CoO nano-composite which was synthesized [26-28], for photocatalytic hydrogen production, where hydrogen production was (830 µmol h^{-1} g^{-1}) for RGO/CoO nano-composite under the visible light.

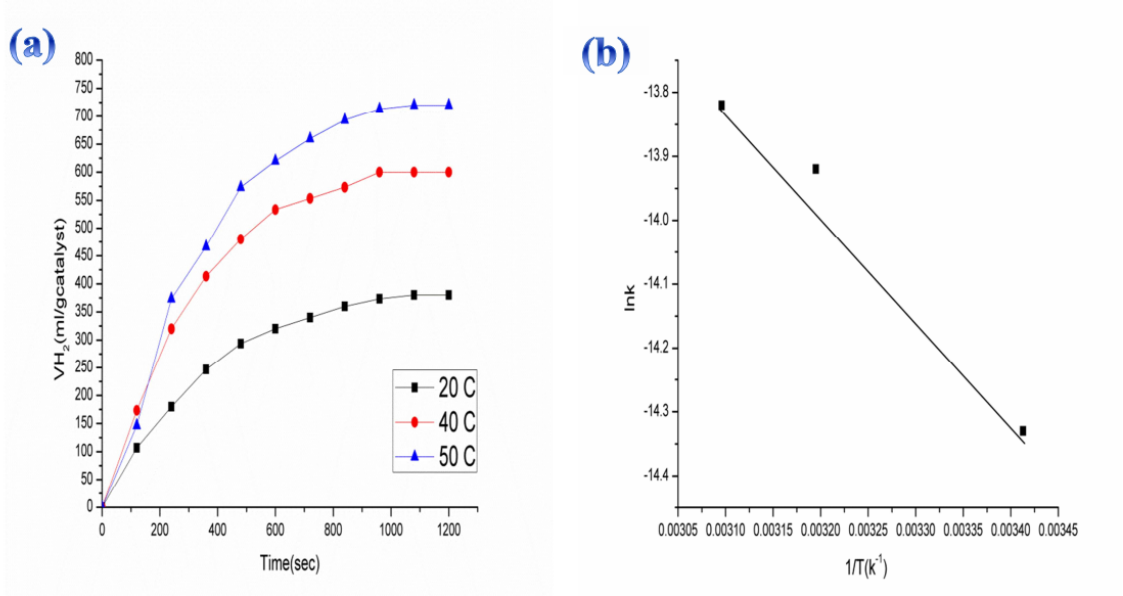

Figure 6. (a) The hydrogen evolution as function of temperature for the optimum ratio of synthesized $ZnCo_2O_4$ nano-catalysts, (Zn: Co) oxide=(1:1.25) .(b) Plot for activation energy determination.

4. Conclusions

$ZnCo_2O_4$ nano-catalysts have been produced by hydrothermal method for the production of hydrogen through photocatalytic water splitting reactions. The characterization confirmed successful synthesis the $ZnCo_2O_4$ nano-catalyst. From the UV-Visible reflectance analysis, the band gap energy was found to be 1.9 eV which is a good indication for the successful synthesis of $ZnCo_2O_4$ nanoparticles with optimal band gap width required for photocatalytic reaction for hydrogen production in the visible range. The photocatalytic activity of the $ZnCo_2O_4$ nano-catalyst towards water splitting for hydrogen generation was examined. The highest hydrogen evolution rate of 19 ml H_2/g. catalyst/min was produced by the optimum ratio of the synthesized $ZnCo_2O_4$ nano-catalysts, (Zn: Co) oxide=(1:1.25).The temperature effect and the kinetic study of photo catalytic water splitting reactions for $ZnCo_2O_4$ nanoparticles, (Zn:Co) oxide=(1:1.25) were discussed and the apparent activation energy was calculated .The photocatalytic activity of $ZnCo_2O_4$ nano-catalyst has been slightly diminished by repeated use, which confirms the catalyst's stability. The impact of the scavenger concentration on photocatalytic water splitting reactions for hydrogen production was also examined and the optimal ratio of Na_2SO_3/Na_2S was found to be 0.5/0.5 M.

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Conflicts of Interest
"The authors declare no conflict of interest." "The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results".

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