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Cr2O3- TiO2 nanocomposite made using plant (Oats) extract via impregnation technique for photocatalytic activity of hydrogen production

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A B S T R A C T

In this study an efficient photocatalyst of water splitting was developed. It's discussed. The Cr2O3 with TiO2nanoparticles (Cr2O3-TNPs) nanocomposite with (Oats extract) were created using ecologically friendly methods impregnation technique such TiO2 exhibits nanospherical (TNPs) shape structure. This nanocomposite material enhanced their ability to absorb ultraviolet light while also speeding up the recombination of photogenerated electrons and holes, according to the researchers. The TNPs and prepared Cr2O3-TNPs were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), energy dispersive x-ray spectroscopy (EDX), and UV-visible absorbance. The XRD of TNPs showed a Tetragonal phase with 8.9 nm of average crystallite size,. FE-SEM images showed that the average particles size in the range of 22.5 nm and UV-VIS absorbance have energy gaps are 3.9eV while the energy gaps of Cr2O3-TNPs smaller than that 3.6 eV. It was found that the performance of photocatalysts of the nanocomposite for hydrogen generation was superior, as it gave the highest rate of hydrogen production (6.3) ml at 80 min when exposed to ultraviolet light. Moreover, the nanocomposite revealed the high H2 production rate under ultraviolt light irradiation ($\lambda < 400$ nm), The Cr2O3-TNps have a high photocatalytic effectiveness due to their wide ultraviolt light photoresponse range and excellent separation of photogenerated electrons and holes.

Keywords **:**Cr2O3-TiO2 nanocomposite; plant extract (Oats); hydrogen production.

1. Introduction

Hydrogen is regarded to be the future's clean energy, capable of resolving global energy and environmental issues. For a long-term hydrogen economy, producing materials that are both efficient and low-cost for H2 production is a fundamental task. Nowadays, natural gas, oil, and coal are used to make hydrogen, which is a scarce and costly resource. Furthermore, creating hydrogen from fossil fuels has the drawback of emitting a significant amount of CO2 [1,2], Concerns about CO2 emissions contributing to global climate change have motivated the development of new environmentally friendly and renewable hydrogen-generation technology. In this case, photocatalysis is a viable approach for producing hydrogen since it can utilize solar energy sustainably and efficiently while also being more cost-effective than more traditional methods[3,4]. In photocatalysis, TiO2 is the most commonly used

semiconductor because of the physical and chemical qualities, as well as its excellent stability, high availability, and low cost [5]. The photocatalytic process involves photon excitation of a semiconductor to generate an electron-hole pair (of appropriate energy - higher or equal to the band gap). Electrons and holes recombine or migrate to the surface of the semiconductor particle, where reduction and oxidation reactions occur. A semiconductor with a conduction band more negative than the H2O/H2 redox couple (0.0 V) and a valence band more positive than the O2/H2O redox couple is required for H2 generation by water splitting (1.23 V versus NHE) at pH = 0. TiO2 (band gap 3.0-3.3 eV) is the semiconductor with the most potential for creating hydrogen from water or biofuels. However, the semiconductor with the most potential for creating hydrogen from biofuels or water. BareTiO2 is ineffective in producing hydrogen, which is often attributed to high hydrogen over potential caused by rapid electron-hole recombination, which reduces the amount of charge-carriers available for the photoreaction. To generate hydrogen, the TiO2 surface must be modified through the use of metal nanoparticles (NPs) of Pt, Pd, Cu, or Cr. Metal's role, according to accepted theories, since metal NPs operate as a drain of electrons, they prevent electron-hole pair recombination[6,7]. However, for hydrogen evolution reactions, another function of metal is also expected, i.e., lowering of over potential of hydrogen evolution, where metal NPs act as a catalyst site for atomic hydrogen formation leading to H2 [8], TiO2 has been modified with transition-metal cations to increase its absorption capacity for light and its photocatalytic capabilities [9,10], Cr2O3 has generally been considered to be a good photocatalytic material for ultraviolet light because of its tight bandgap, and thus, it has been considered as a TiO2 dopant [10,11]. Cr3+ was mixed into TiO2 powder to increase its photocatalytic capabilities[12], several studies have suggested adding chromium oxide to titanium oxide and improving the effectiveness of photocatalysis [13]. In this study, chromium oxide (Cr2O) with plant (Oats) extract were loaded on titanium oxide (TiO2) to obtain a Cr2O3-TiO2 nanocomposite using impregnation technique. It is possible to detect some of the plant's most important constituents in the plant extract (Oats), including the molecule β-glucan (a mixed-linkage polysaccharide that is an important part of oat fiber and contains avenanthramides, an indole alkaloid-gramine, flavonoids, and other phytoconstituents such as these)[14], which are important components of the Oats extract .Plant extract (Oats) was used to synthesize Cr2O3-TiO2 , Cr(NO3)3.9H2O solution was used as a Cr precursor to the β-glucan, the hydroxyl and naphthoquinone groups may cause Cr3+ reduction and stabilization of the Cr2O3-TiO2 nanocomposite. The OH team has a significant impact on reduction. To reduce Cr(NO3)3 hydroxide, Oats extract partially reduces Cr(NO3)3 hydroxide to generate Cr2O3-TiO2 nanocomposite, The objectives of this work are synthesise Cr2O3-TiO2 nanocomposite to improve photogenerated electron–hole pair efficiency and photocatalytic activity by improving optical responsiveness in ultraviolet range.

2. Experimental part

2.1. Preparation of the plant extract (Oats)

0.5 gm. oats dispersed in 50ml deionized water with an ultrasonic assistant at 60 ^{o}C for 45 minutes to produce a white, transparent solution. After cooling to room temperature, the extract was filtered using Whatman filter paper No. 0.5 and cleared several times by the centrifuge at 4000 rpm for 5 minutes to remove any residual salts and impurities.

2.2. Preparation of the Cr_2O_3-TiO_2 nanocomposites using plant extract (Oats)

Cr_2O_3-TiO_2 nanocomposite was synthesise using 0.0329 gm. of $Cr(NO_3)_3.9H_2O$ with 2 ml from anhydrous ethanol solution and 1 ml of plant extract (oats) treated with ultrasonic assistance to produce a clear dark blue solution that was then impregnated with 2.5 gm Commercial TiO_2 nanoparticles were purchased from Sky spring Nanomaterial. The impregnate was volatilized at 70°C until being annealed for 2 hours at 300°C. A gree with [15].

2.3. Characterization of Cr_2O_3-TiO_2 nanocomposites

Characterization of TiO_2 nanoparticls(TNPs), Cr_2O_3-TNPs, were carried out by different techniques. UV–visible spectrophotometer type (DU- 8800D- China) within range (200-900) nm. The morphological properties was examined used Field Emission Scanning Electron Microscopy (FESEM INSPECT F-50, Company FEI, Dutch) with energy dispersive (X-Ray) spectroscopy (EDX). X-Ray diffraction was recorded with a SHIMADZU, (XRD - 6000, JAPAN) using CuKα radiation (λ=1.5406 Å).

2.4. The assessment of photocatalytic hydrogen generation

As shown in figure 1, the laboratory cell that was used to separate hydrogen from water was made locally from quartz glass (6cm x 28cm) of hydrogen gas cylinder. Where the cylinder is equipped with holes for the exit of gas, Water decomposition was carried out using an analytical system, such the quantity of photocatalyst that measured was (2 gm) from compsite Cr_2O_3/TiO_2 placed in a quartz flask containing (500ml) water and 0.028 M of KOH of a sacrificial reagent aqueous solution (Cr_2O_3-TiO_2) which it exposed using ultraviolet light irradiation (λ<400nm).

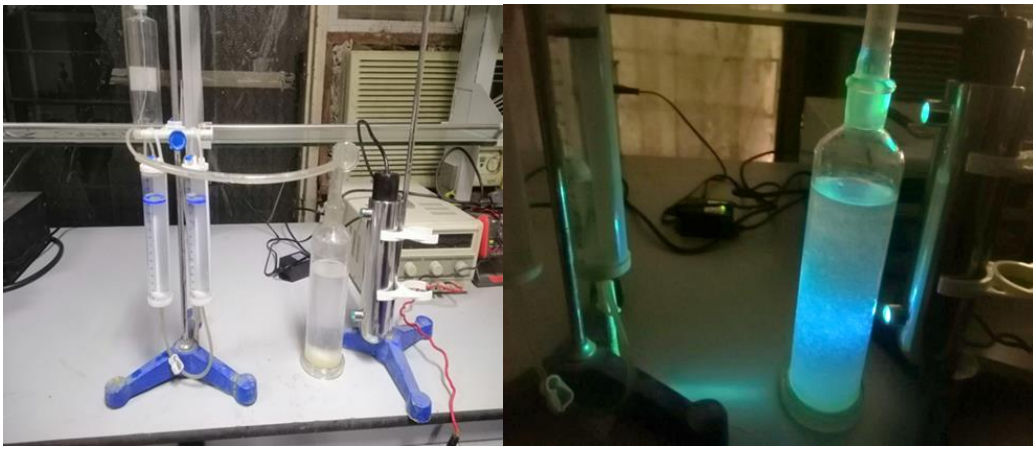

Figure 1: Shows a laboratory hydrogen separation system

3. Results and discussion

3.1 XRD analysis of pure TNPs and Cr2O3 -TNPs nanocomposite

The XRD pattern of TNPs reveal the plane (101), (103), (004), (112), (200), (105), (211), (204), and (116) have values of 2θ (25.2°), (36.9°), (37.8°), (38.3°), (48.2°), (53.7°), (55.2°), (62.6°), and (68.2°) respectively as shown in figure 2. The diffraction peaks reveal a tetragonal anatase phase, according to (JCPDS No..84-1285). The strongest diffraction peak at 24.8 indicated to (101) plane of anatase TiO2, the anatase structure is responsible for the peaks other than (53.7°), and (55.2°), while the rutile structure is also responsible for the peaks (53.7°) and (55.2°), this indicates that anatase is the dominant crystal phase in TiO2 nanoparticles, with the presence of some rutile phases in small amounts in the final product. These findings are consistent with earlier research by[16], The average crystallite size, founded by Scherer's formula [13] is equal to 8.9nm of TNPs.

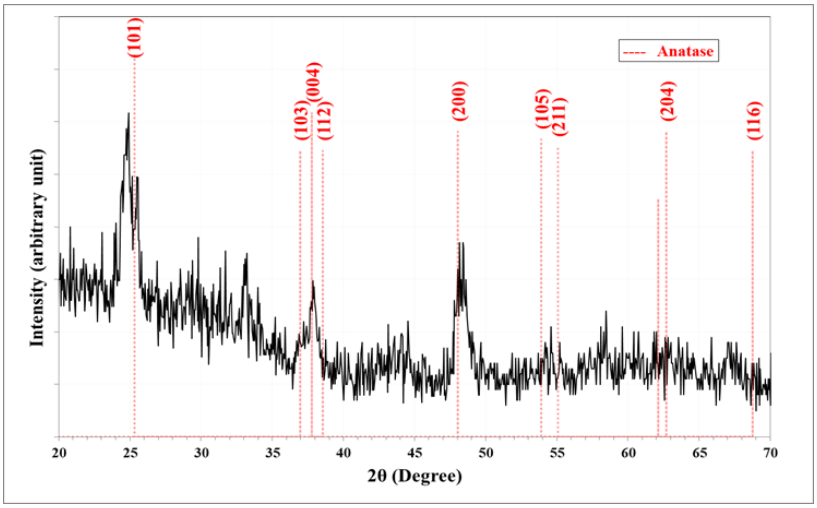

Figure 2: XRD patterns of TNPs

Figure 3 illustrate the XRD spectra of Cr2O3-TNPs nanocompasite heterostructures at different Cr2O3 percentages. Diffraction plane (101), (104), (103), (004), (112), (202), (200), (105), (211), (204), and (116) (JCPDS Card NO. 84-1285), corresponding to 2θ = (25.5 °), (36.8°), (37.9°), (38.3°), (48.2°), (53.9°), (55.2°), (62.7°) and (68.7°) are seen in the crystallized anatase phase of Cr2O3-TNPs. Because the small proportions of Cr2O3 particles rlative to TiO2 ratio the XRD result appears the tiny peaks of Cr2O3 at 2θ = (33.6°), and (44.2°) (JCPDS No. 1308-38-9). According to these findings, the successful modification of titanium dioxide with amount of Cr2O3 has created flaws in the anatase crystal to form Ti-O-Cr bonds which allows it to interact with both Cr3+ ions and TiO2[14]. As a result, it is conclud that the pore wall of TiO2 is blocked by the presence of Cr2O3.The crystal size of Cr2O3-TNps is 13.5 nm.

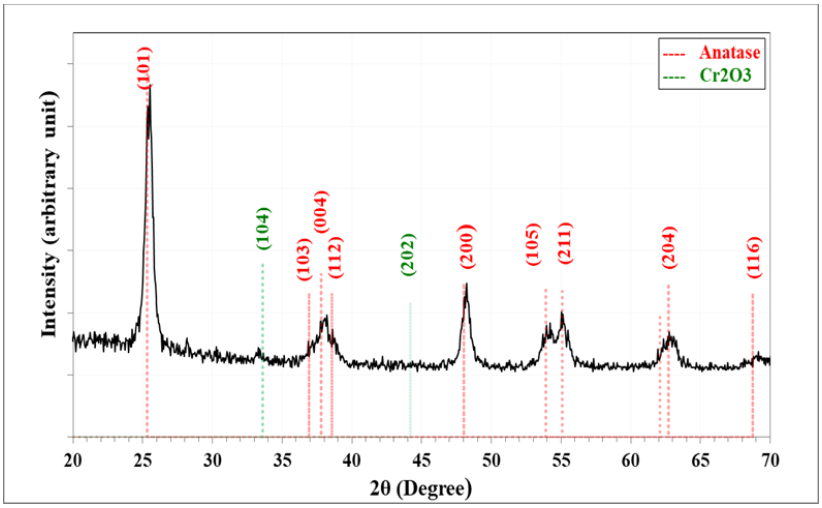

Figure 3: XRD patterns of Cr2O3-TNPs nanocomposites.

3.2 FE-SEM images of pure TNPs and Cr_2O_3-TNPs nanocomposites

The morphology of pure TNPs in figure (4-A) appears as a semi-spherical, with an average particle size of 22.5 nm (measured using Image J software), Figure (4-B) show Cr_2O_3 with TNPs with an average particle size 35 and exhibited the agglomeration of nanoparticles and the formation of a wide surface area [14], where the bonding of chromium and titanium oxide particles by weak forces led to these agglomeration

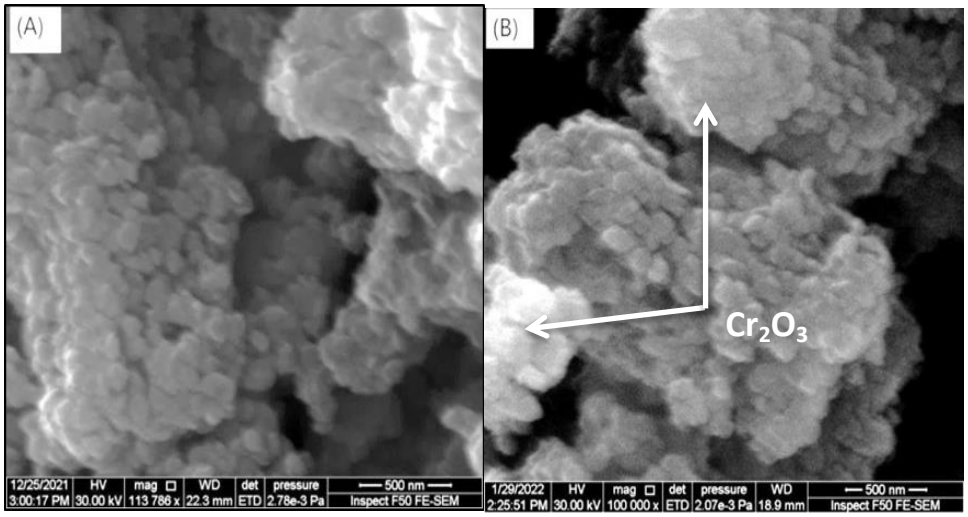

Figure 4: FE-SEM images of (A)pure TNPs.(B) Cr_2O_3 -TNPs composite

3.3.EDX of of TNPs and Cr_2O_3-TNPs nanocomposites

EDX analyses of TNPs and Cr_2O_3 with TNPs nanocompsite are shown in figures 5 and tables 1. It reveals the characteristic emission peaks for Ti ,O_2 and Cr elements, there are some trace elements observed in both samples as a residual from the extract material.

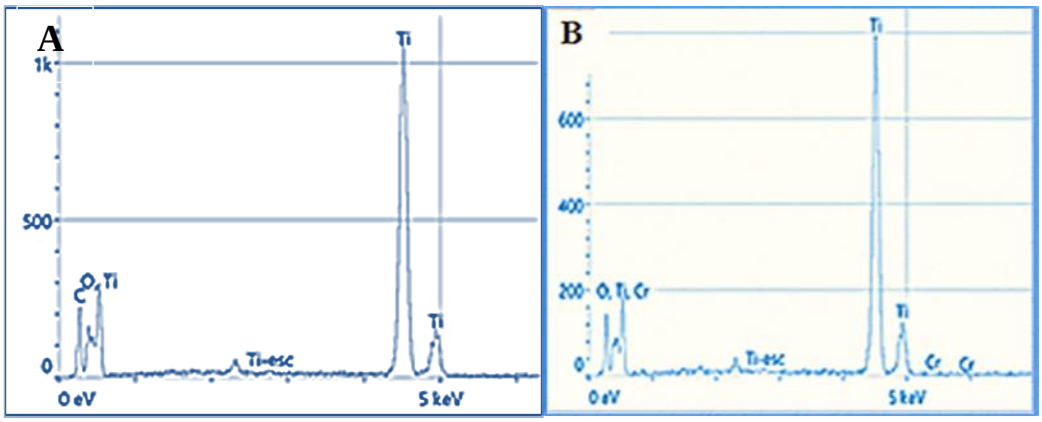

Figure 7: The elements, atomic and weight ratios of (A) TNPs (B) Cr2O3 with TNPs nanocomposite

Table 1: The elements, atomic and weight ratios of TNPs And Cr2O3 with TNPs

Element	TNPs		Cr_2O_3 with TNPs	
	Atomic %	Weight %	Atomic%	Weight %
O	18.0	41.5	71.4	45.4
Ti	57.3	44.2	28.5	54.3
C	24.7	14.3	_____	_____
Cr	_____	_____	0.2	0.3

3.4 Ultraviolet Visible (UV-Vis) properties of TNPs and Cr_2O_3-TNPs nanocomposite

Figure 8 depicts the UV-visible absorption spectra of samples where TNPs sample absorption edge is located at 300 nm, the Tauc formula was used to determine the energy gap, which is equal to 3.9 eV for the TNPs, the absorption edge is sharp. We note its stability in absorption at the $\lambda >=350$ nm, this means that the energy of photon is low and does not cause excite electrons from the valance band to the conduction band but at short wavelengths, the photon energy is increase and electrons exited to conduction band ,this leads to absorption. As shown in Figure 9. Figure10 appear that Cr^{3+} loading into TNPs improves their absorption in the ultraviolet region, the absorption edge of Cr_2O_3-TNPs is appearing at 336 nm and the energy gap is equal to 3.6eV as shown in figure11. The absorption edge of the Cr_2O_3-TNPs nanocomposite with oats extract shifted to the greater wavelength in the ultra-violet as compared to the pure TNPs, it may be concluded that proper Cr resulted in the narrowing of the anatase TiO_2 band gap. The introduction of dope levels is to cause for the narrower bandgap. This would also cause an electron to be excited from the valence band to the dope levels, Cr doping may also act as an electron-capture trap, preventing recombination of electron-hole pairs and Cr doping, on the other hand, produces deep dope levels, which are recombination sites that can speed up the recombination of electron-hole pairs., therefore, these agreed from [17].

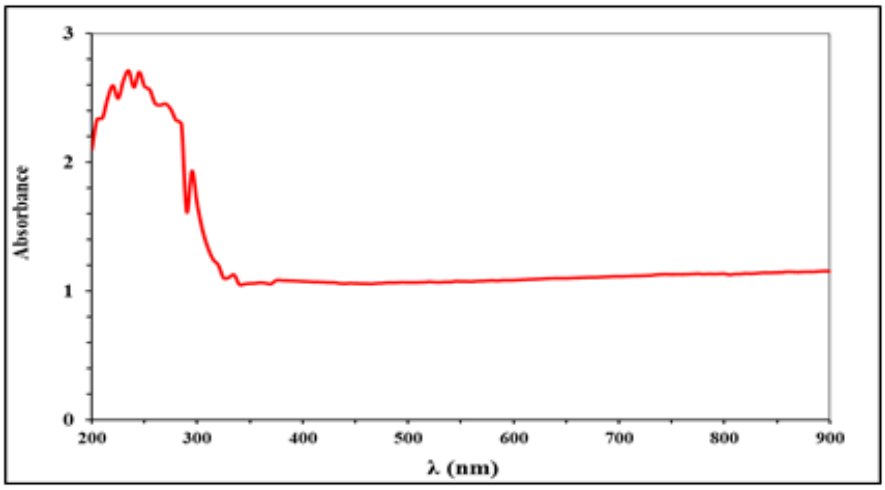

Figure8: Ultraviolet-visible absorption spectra of pure TNPs

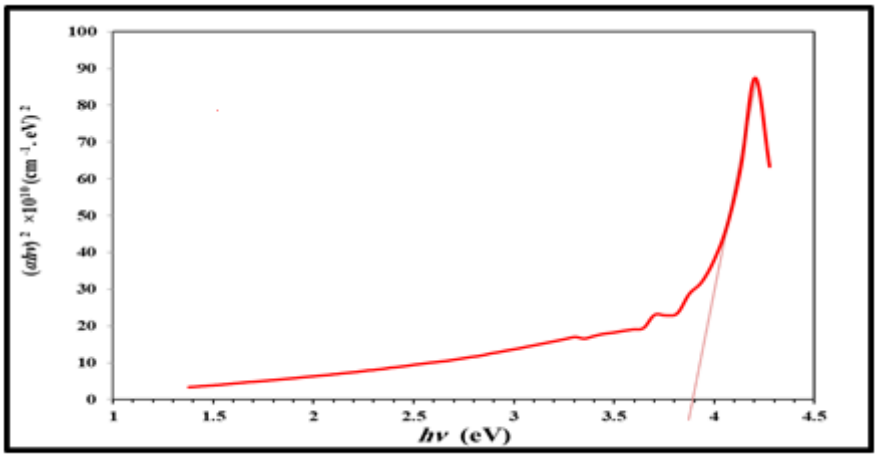

Figure 9: The energy gap of pure TNPs.

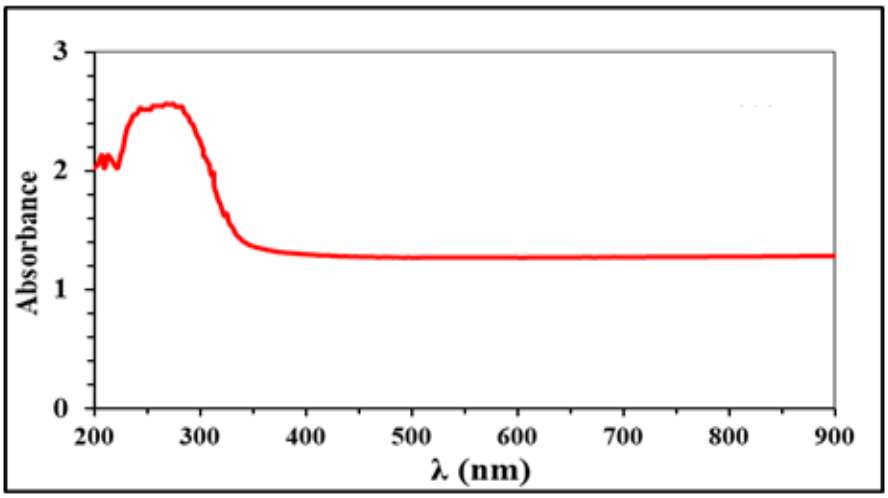

Figure 10: Ultraviolet-visible absorption spectra of Cr2O3-TNPs nanocomposite

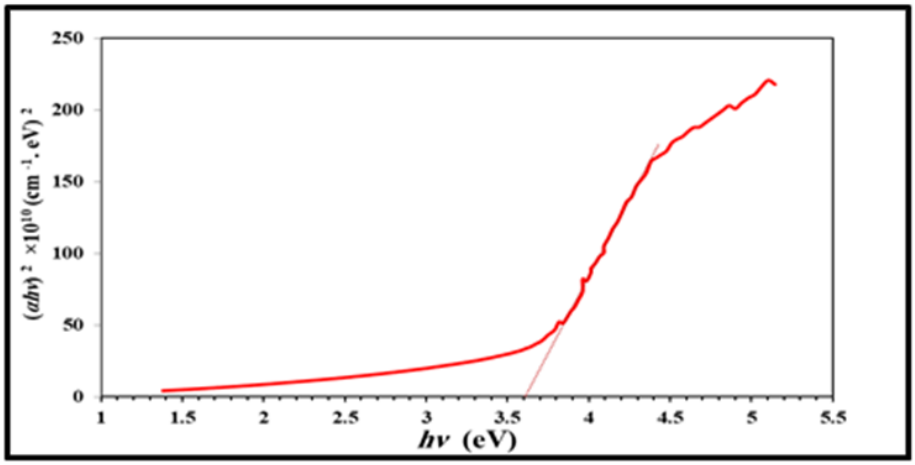

Figure 11: The energy gap of Cr_2O_3-TNPs.

3.5. Activity of hydrogen production

The photocatalytic decomposition of water under ultraviolet light irradiation generated hydrogen for Cr_2O_3 –TNPs. The average hydrogen generation for Cr_2O_3-TNPs at different times (10 - 80) min are summarized in figure (12) and table (2), it was observed that the hydrogen is not produced in the first 10 min of the reaction and the lowest production of hydrogen was (0.4) ml at 20 min and the highest production of hydrogen at 80 min was (6.3) ml. The effectiveness of the components (such as salts and oxides of transition metals) for many catalysts is spontaneously dispersed on the surface of the carriers, where hydrogen gas is produced in a volume twice the size of oxygen gas through as well as the photocatalyst, an increase in hydrogen production was observed due to the photocatalysts effect on the reaction speed. The work of the photocatalyst must comply with many basic principles to obtain an efficient hydrogen production process, meaning that the best photocatalyst for hydrogen production is the one with the highest quantitative yield and the highest gaseous production rate. The main measure of photocatalyst action is quantitative.

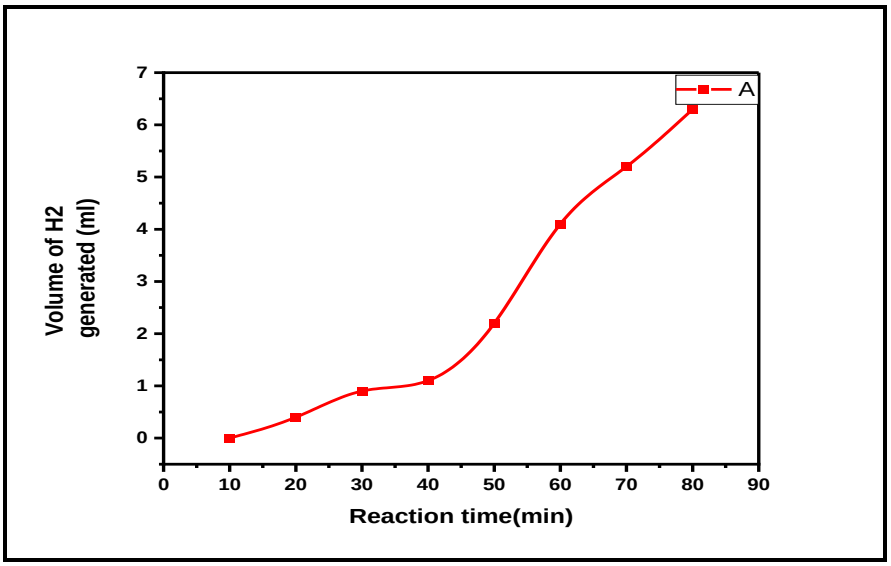

Figure (12): Time courses of hydrogen evolution over Cr_2O_3-TNPs

Table (2): Summary volume of H_2 production (ml) and reaction time of Cr_2O_3 –TNPs photocatalysts, it is measured by liquid displacement

Volume of H_2 generated (ml)	Reaction time(min)
0	10
0.4	20
0.9	30
1.1	40
2.2	50
4.1	60
5.2	70
6.3	80

4. Conclusions

Impregnation processes were used to create of Cr_2O_3-TiO_2 nanocomposites. An XRD and FESEM analysis of nanocomposites showed that they contained a mixture of Cr_2O_3-TiO_2 (nano semispherical). The average diameter of the nanoparticles 22.5nm for pure TNPs, the absorption edge of TNPs can be extended to the ultraviolet range was 300 nm and the energy gap is equal to 3.9 eV is larger than the energy gap of Cr_2O_3-TNPs is equal to 3.6eV because of the appropriate Cr doping resulted in narrowing of the band gap of the anatase TiO_2. Briefly, it has succeeded in synthesizing environmentally friendly biomolecules via impregnation method. If the effect of the morphology of the compound Cr_2O_3-TNPs was in the form of semi spherical, it was discovered to have an effect on the performance of the current work, where the compound Cr_2O_3-TNPs showed a distinguished performance in hydrogen production through photocatalysts .The average hydrogen generation rates for the Cr_2O_3-TNPs sample by photocatalytic decomposition of water at (2gm) from composite under UV light irradiation at different times (10, 20, 30, 50, 60, 70, 80) min. As shown in figure (12) and table(2) , it is observe the hydrogen is not produced in the first 10 min of the reaction , the lowest production of hydrogen is evolve 0.4 ml at 20 min and the highest production of hydrogen at 80 min are 6.3 ml using oats extract. Presence of Cr_2O_3 significantly enhances the efficiency of hydrogen production resulting from the effective charge separation in Cr_2O_3-TiO_2 photocatalysts, as the separation and transfer of charges in the Cr_2O_3-TiO_2 nanocomposite is crucial and important in the efficiency of hydrogen production. The hydrogen production increases with increasing time. We conclude from the above, the nanocomposite's ability to make hydrogen is largely dependent on the amount of Cr^{3+} that can be added to the TNPs.

5. References

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