Producing Hydrogen Energy Using Cr$_2$O$_3$-TiO$_2$ Nanocomposite with Animal (Chitosan) Extract via Photocatalysis

**Ghasaq Z. Alwan**  
Department of Physics, College of Education Mustansiriyah University, Baghdad, Iraq.  
Gasaq.zuher@gmail.com

**Wisas J. Aziz**  
Department of Physics, College of Education Mustansiriyah University, Baghdad, Iraq.  
wisamjafer14@gmail.com

**Raad S. Sabry**  
Department of Physics, College of Education Mustansiriyah University, Baghdad, Iraq.  
raadsaodon74@gmail.com

**Article history:** Received 8 May 2022, Accepted 14 June 2022, Published in October 2022.

**Doi:** 10.30526/35.4.2853

**Abstract**

In this study, an efficient photocatalyst for water splitting was developed. The Cr$_2$O$_3$ and TiO$_2$ nanoparticles (Cr$_2$O$_3$-TNPs) nanocomposite with (Chitosan extract) was created using ecologically friendly methods, such as the impregnation technique as TiO$_2$ exhibits nano spherical (TNPs) shape structure. According to the researchers, this nanocomposite material enhanced its ability to absorb ultraviolet light while also speeding up the recombination of photogenerated electrons and holes. The TNPs and prepared Cr$_2$O$_3$-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 and 14.2 nm for nanocomposite. FE-SEM images showed that the average particle size in the range of (12.5-57.5) nm and UV-VIS absorbance has energy gap of 3.8 eV, while the energy gap of Cr$_2$O$_3$-TNPs is 2.8 eV. It was found that the performance of photocatalysts of the nanocomposite for hydrogen generation was superior. It gave the highest rate of hydrogen production (3.6) ml at 80 min when exposed to ultraviolet light. Moreover, the nanocomposite revealed high H$_2$ production rate under ultraviolet light irradiation ($\lambda < 400$ nm). The Cr$_2$O$_3$-TNPs have high photocatalytic effectiveness due to their wide ultraviolet light photoresponse range and excellent separation of photogenerated electrons and holes.

**Keywords:** Cr$_2$O$_3$-TNPs nanocomposite; chitosan extract; hydrogen production; photocatalyst.
1. Introduction

Hydrogen has the potential to be a powerful energy carrier and an appropriate energy storage material to substitute fossil fuels, a wealth of natural resources such as biomass and water [1][2]. Photocatalytic water splitting, in particular, is being investigated as a possible approach for producing hydrogen using solar light [3]. Various inorganic or organic semiconductors have been explored over the last 40 years. However, it has primarily been used in the water splitting half-reaction example as the oxidation of water to oxygen (O$_2$) or the reduction of protons to hydrogen (H$_2$) [4][5]. The limitations of water splitting in pure water over a semiconductor are limited effective separation of photogenerated carriers and the rapid H$_2$-O$_2$ recombination reverse reaction [6][7]. In this case, photocatalysis is a viable method for producing hydrogen because it can utilize solar energy in a cost-effective and environmentally friendly process while also being more cost-effective than traditional methods. However, society not only provides comfort and well-known technology but also comes with the well-known disadvantage of CO$_2$ release. Most combustion activities produce this gas, which is thought to be the primary cause of global warming since global industrialization has risen by a significant amount [8].

Hydrogen widely believed to be the most potential clean energy carrier for the future and whose usage is being researched in many technology sectors, is an appealing alternative to fossil fuels as an energy source [9]. Water is a natural source of hydrogen and oxygen, and over the last few decades been a surge in interest in using photocatalysis to split water and make H$_2$ [10]. In photocatalysis, TiO$_2$ is the most commonly used semiconductor because of its physical and chemical qualities, as well as its wide availability, outstanding stability, inexpensive cost [11], alternation of the surface [12][13], co-catalysts for loading [14][15], heterojunctions creation [16][17]. The photocatalytic process involves photon excitation of a semiconductor to generate 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 H$_2$O/H$_2$ redox couple (0.0 V) and a valence band more positive than the O$_2$/H$_2$O redox couple is required for H$_2$ generation by water splitting (1.23 V versus NHE) at pH = 0. TiO$_2$ (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 is biofuels or water. Bare TiO$_2$ is ineffective in producing hydrogen.

It is often attributed to high hydrogen over potential caused by rapid electron-hole recombination. TiO$_2$ has been modified with transition-metal cations to increase its absorption capacity for light and its photocatalytic capabilities [18][19]. Cr$_2$O$_3$ is generally considered an excellent photocatalytic material for ultraviolet light because of its tight band gap; thus, it has been considered a TiO$_2$ dopant [19][20]. Cr$^{3+}$ was mixed into TiO$_2$ powder to increase its photocatalytic capabilities [21]. Several studies have suggested adding chromium oxide to titanium oxide and improving the effectiveness of photocatalysis [22]. In this study, chromium oxide (Cr$_2$O) with animal (chitosan) extract was loaded on titanium oxide (TiO$_2$) to obtain a Cr$_2$O$_3$-TiO$_2$ nanocomposite using the impregnation technique. It is possible to detect some of the essential constituents in the animal extract (chitosan), including preliminary totals found in the rutin (Rutin is a rutinoside that is quercetin with the hydroxy group at position C-3 replaced by glucose and rhamnose sugar groups) vitamin C.

Cellulose is also included in chitosan, a significant component of the chitosan extract [23]. Animal extract (chitosan) was used to synthesize Cr$_2$O$_3$-TiO$_2$. The OH team has a significant impact on
reduction. To reduce Cr(NO₃)₃ hydroxide, chitosan extract partially reduces Cr(NO₃)₃ hydroxide to generate Cr₂O₃-TiO₂ nanocomposite. This work aims to synthesize the Cr₂O₃-TiO₂ nanocomposite to improve photogenerated electron-hole pair efficiency and photocatalytic activity by improving optical responsiveness in the ultraviolet range.

2. Materials and Methods

2.1. Preparation of the Animal Extracts (chitosan)

0.5 gm. of chitosan was dissolved in 1:50 acetic acid with water ratio and ultrasonically mixed for 2 h, then filtered using a micro porous membrane (pore size. Μm) 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 Cr₂O₃-TiO₂ nanocomposites

Cr₂O₃-TiO₂ nanocomposite was synthesized using 0.0329 gm. of Cr(NO₃)₃·9H₂O with 2 ml from anhydrous ethanol solution and 1 ml of chitosan extract treated with ultrasonic assistance to produce a clear dark blue solution that was then impregnated with 2.5 gm. Commercial TiO₂ nanoparticles were purchased from Sky spring Nanomaterial. The impregnate was volatilized at 70°C until being annealed for 2 hours at 300°C.

2.3. Characterization of Cr₂O₃-TiO₂ nanocomposites

Characterization of TiO₂ nanoparticles (TNPs), and Cr₂O₃-TNPs were carried out by different techniques. UV–visible spectrophotometer type (DU- 8800D- China) within the range (190-1100) 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 used to separate hydrogen from the water was made locally from a hydrogen gas cylinder quartz glass (6cm x 28cm). The cylinder is equipped with holes for the exit of gas. Water decomposition was carried out using an analytical system, such as the quantity of photocatalysts. 2 gm of Cr₂O₃/TiO₂ placed in a quartz flask containing (500 ml) water and 0.028 M of KOH of a sacrificial reagent aqueous solution (Cr₂O₃-TiO₂) which exposed using ultraviolet light irradiation (λ<400nm).

![Figure 1: Laboratory hydrogen separation system.](image-url)
3. Results and dissection

3.1 XRD analysis

The XRD pattern of TNPs reveals the planes (101), (103), (004), (112), (200), (105), (211), (204), and (116) assigned at 2θ of (24.8°), (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 TiO$_2$. 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 TiO$_2$ nanoparticles, with the presence of some rutile phases in small amounts in the final product. These findings are consistent with earlier research by[24]. The average crystallite size, founded by Scherer's formula [22], equals to 8.9 nm of TNPs.

![Figure 2.XRD patterns of TNPs](image)

Figure 3 illustrates the XRD spectra of Cr$_2$O$_3$-TNPs nanocomposite heterostructures at different Cr$_2$O$_3$ percentages. Diffraction planes (101), (104), (103), (004), (112), (202), (200), (105), (211), (204), and (116) (JCPDS Card NO. 84-1285), corresponding to 2θ = (24.7°),(36.5°),(37.8°), (38.1°), (47.9°), (53.8°), (55.5°), (62.7°) and (68.5°) are seen in the crystallized anatase phase of Cr$_2$O$_3$-TNPs. Because of the small proportions of Cr$_2$O$_3$ particles relative to the TiO$_2$ ratio, the XRD result appears the tiny peaks of Cr$_2$O$_3$ at 2θ = (33.1°) and (44.2°) (JCPDS No. 1308-38-9). According to these findings, the successful modification of titanium dioxide with the amount of Cr$_2$O$_3$ has created flaws in the anatase crystal to form Ti-O-Cr bonds which allow it to interact with both Cr$^{3+}$ ions and TiO$_2$. As a result, it is concluded that the presence of Cr2O3 blocks the pore wall of TiO2. The crystal size of Cr$_2$O$_3$-TNPs is 14.2 nm.
3.2 FE-SEM images of TNPs and Cr$_2$O$_3$-TNPs nanocomposites

The morphology of TNPs in figure (4-A) appears as semi-spherical, with an average particle size of 12.5-57.5 nm (measured using Image J software). Figure (4-B) shows Cr$_2$O$_3$ with TNPs where exhibited the agglomeration of nanoparticles and the formation of a wide surface area [25], where the bonding of chromium and titanium oxide particles by weak forces led to these agglomerations.
3.3. EDX of TNPs and Cr$_2$O$_3$-TNPs nanocomposites

EDX analyses of TNPs and Cr$_2$O$_3$ with TNPs nanocomposite are shown in Figure 5 and Table 1. It reveals the characteristic emission peaks for Ti and O$_2$, in addition to C and some trace elements observed in both samples as a residual that comes from the extracted material. The presence of phytomolecules (polyphenols, alkaloids, and flavonoids) of chitosan is extracts adsorbed on the TNPs surface.

![Figure 5](image)

**Figure 5.** The elements, atomic and weight ratios of (A) TNPs (B) Cr$_2$O$_3$ with TNPs nanocomposite with Chitosan

**Table 1.** The elements, atomic and weight ratios of TNPs and Cr$_2$O$_3$ with TNPs

<table>
<thead>
<tr>
<th>Element</th>
<th>TNPs</th>
<th>Cr$_2$O$_3$ with TNPs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atomic %</td>
<td>Weight %</td>
</tr>
<tr>
<td>O</td>
<td>18.0</td>
<td>41.5</td>
</tr>
<tr>
<td>Ti</td>
<td>57.3</td>
<td>44.2</td>
</tr>
<tr>
<td>C</td>
<td>24.7</td>
<td>14.3</td>
</tr>
<tr>
<td>Cr</td>
<td>______</td>
<td>______</td>
</tr>
<tr>
<td>S</td>
<td>______</td>
<td>______</td>
</tr>
<tr>
<td>N</td>
<td>______</td>
<td>______</td>
</tr>
</tbody>
</table>
3.4 Ultraviolet Visible (UV-Vis)

Figure 6 depicts the UV-visible absorption spectra of samples where the TNPs sample absorption edge is located at 300 nm. The Tauc formula was used to determine the energy gap equal to 3.8 eV for the TNPs, as shown in Figure 7.

Figure 8 shows that Cr$^{3+}$ loading into TNPs improves their absorption in the UV-Visible region, the absorption edge of Cr$_2$O$_3$-TNPs appears at 415 nm, and the energy gap is equal to 2.8 eV, as shown in figure 9. The absorption edge of the Cr$_2$O$_3$-TNPs nanocomposite with chitosan extract shifted to a greater wavelength in the visible region as compared to the undoped TNPs. It may be concluded that proper Cr doping resulted in the anatase TiO$_2$ band gap narrowing. The introduction of dope levels is to cause a narrower band gap. 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 the recombination of electron-hole pairs. On the other hand, Cr doping produces deep dope levels and recombination sites that can speed up the recombination of electron-hole pairs [26].

![Figure 6](image1.png)

**Figure 6.** Ultraviolet-visible absorption spectra of TNPs.

![Figure 7](image2.png)

**Figure 7.** The energy gap of TNPs.
3.5. Activity of hydrogen production

The photocatalytic decomposition of water under ultraviolet light irradiation generated hydrogen for Cr₂O₃ –TNPs. The average hydrogen generation for Cr₂O₃-TNPs at different times (10 - 80) min are summarized in Figure (10) and Table (2), it was observed that the hydrogen was not produced in the first 10 min of the reaction. The lowest hydrogen production was (0.2) ml at 20 min and the highest hydrogen production at 80 min was (3.6) 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 effect photocatalysts 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 (10). Time courses of hydrogen evolution over \( \text{Cr}_2\text{O}_3\text{-TNPs} \) with chitosan extract.

Table (2). Volume of hydrogen generated (ml) and reaction time of (Cr\(_2\)O\(_3\)-TNPs).

<table>
<thead>
<tr>
<th>Cr(_2)O(_3)-TNPs Volume of hydrogen generated (ml)</th>
<th>Reaction time(min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>0.2</td>
<td>20</td>
</tr>
<tr>
<td>0.76</td>
<td>30</td>
</tr>
<tr>
<td>1.0</td>
<td>40</td>
</tr>
<tr>
<td>1.4</td>
<td>50</td>
</tr>
<tr>
<td>1.9</td>
<td>60</td>
</tr>
<tr>
<td>3.0</td>
<td>70</td>
</tr>
<tr>
<td>3.6</td>
<td>80</td>
</tr>
</tbody>
</table>

5. Conclusion

Impregnation processes were used to create \( \text{Cr}_2\text{O}_3\text{-TiO}_2 \) nanocomposites. XRD and FESEM analysis of nanocomposites showed that they contained a mixture of \( \text{Cr}_2\text{O}_3\text{-TiO}_2 \) (nanospherical). The average diameter of the nanospherical was (12.5-57.5) nm. The absorption edge of TNPs can be extended to the ultraviolet range was 300 nm, and the energy gap is equal to 3.8 eV is larger than the energy gap of \( \text{Cr}_2\text{O}_3\text{-TNPs} \) is equal to 2.8eV because the appropriate Cr doping resulted in a narrowing of the band gap of the anatase TiO\(_2\). Briefly, it has succeeded in synthesizing environmentally friendly biomolecules via the impregnation route. If the effect of the morphology of the compound \( \text{Cr}_2\text{O}_3\text{-TNPs} \) was in the form of spherical, it was discovered to have an effect on the performance of the current work, where the compound \( \text{Cr}_2\text{O}_3\text{-TNPs} \) showed a distinguished performance in hydrogen production through photocatalysts and increased with increasing time, the highest production at the 80 min, it was (3.6) ml. We conclude from the above that the nanocomposite's ability to make hydrogen largely depends on the amount of Cr\(_3^+\) that can be added to the TNPs.
References


16. Li, H.; Zhou, Y.; Tu, W.; Ye, J.; and Zou, Z.; State-of-the-art progress in diverse


18. Wang B.; Cr2O3@ TiO2 yolk/shell octahedrons derived from a metal–organic framework for high-performance lithium-ion batteries, *Microporous Mesoporous Mater.*, 2015. 203, 86–90,

19. Huang H.; Design of twin junction with solid solution interface for efficient photocatalytic H2 production, *Nano Energy*, 2020. 69, 104410,


