Producing Hydrogen Energy Using Cr\textsubscript{2}O\textsubscript{3}-TNFs Nanocomposite with Animal (Chitosan) Extract via Ultrasonic and Hydrothermal Techniques

Ghasaq Z. Alwan\textsuperscript{a*}, Wisam J. Aziz\textsuperscript{b} and Raad S. Sabry\textsuperscript{c}

\textsuperscript{a}Department of Physics, College of Science, University of Mustansiriyah, Baghdad, Iraq
\textsuperscript{b}E-mail: wisamjafer14@gmail.com, E-mail: raadsaadon74@gmail.com
\textsuperscript{c}Corresponding Author: Gasaq.zuher@gmail.com

Abstract
In this study, an efficient photocatalyst for dissociation of water was prepared and studied. The chromium oxide (Cr\textsubscript{2}O\textsubscript{3}) with Titanium dioxide (TiO\textsubscript{2}) nanofibers (Cr\textsubscript{2}O\textsubscript{3}-TNFs) nanocomposite with (chitosan extract) were synthesized using ecologically friendly methods such as ultrasonic and hydrothermal techniques; such TiO\textsubscript{2} exhibits nanofibers (TNFs) shape structure. Doping TiO\textsubscript{2} with chromium (Cr) enhances its ability to absorb ultraviolet light while also speeding up the recombination of photogenerated electrons and holes. The prepared TNFs and Cr\textsubscript{2}O\textsubscript{3}-TNFs 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 TNFs showed a tetragonal phase with 6.9 nm of average crystallite size, whereas Cr\textsubscript{2}O\textsubscript{3}-TNFs crystallite size was 12.3 nm. FE-SEM images showed that the average particle size of TNFs was in the range of (9-35) nm and UV-Vis absorbance of TNFs showed their energy gap to be 3.9eV while the energy gaps of Cr\textsubscript{2}O\textsubscript{3}-TNFs were smaller equal to 2.4 eV. The highest hydrogen production rate for the Cr\textsubscript{2}O\textsubscript{3}-TNFs nanocomposite was 4.1ml after 80min of UV exposure. Cr\textsubscript{2}O\textsubscript{3}-TNFs have high photocatalytic effectiveness due to their wide ultraviolet light photoresponse range and excellent separation of photogenerated electrons and holes.

Keywords: Cr\textsubscript{2}O\textsubscript{3}-TNFs nanocomposite, chitosan extract, hydrothermal technique, photocatalyst, hydrogen production.

1. Introduction
Fossil fuel usage has recently become a source of concern, both in terms of its existence and its long-term viability, as well as its impact on the environment. Alternative energy sources that are renewable and eco-friendly are required for future community growth. The sun is the world's largest and most affordable (free) energy source. It has the potential to be a renewable energy source. Various technologies for solar energy conversion and usage have been tested. Solar energy has long been regarded as the most efficient and environmentally friendly method of producing hydrogen. Fuel cells can use the hydrogen, produced from the splitting of water using solar energy to generate energy. The efficiency of solar water separation device become the primary fuel for a renewable energy economy, must be enhanced if solar energy will play a significant role in the production of clean fuels (hydrogen). In order for hydrogen to become the primary fuel for a renewable energy economy in the future, high-capacity hydrogen storage technology and high-performance fuel cells, must be created [1]. In this case, photocatalytic water splitting into O\textsubscript{2} and H\textsubscript{2} is a viable option [2]. Because of its zero-emissions and long-term viability, hydrogen is highly regarded as a fuel. Titanium dioxide (TiO\textsubscript{2}) has long been the most extensively used photocatalyst for hydrogen generation because of its stability, corrosion resistance, purity (no contaminates), natural availability, and low cost [3, 4]. The photocatalytic activity of TiO\textsubscript{2} has been reported to be improved by heteroatom doping [5], alternation of the surface [6, 7], co-catalysts for loading [8, 9], and
heterojunctions creation [10, 11]. It has substantial band-gap energy (anatase 3.2 eV and rutile 3.0 eV). Under UV light irradiation, TiO$_2$ has been widely employed as a photocatalyst for photocatalytic water splitting to create hydrogen [12]. UV light stimulates electrons from the valence band into the conduction band, resulting in the formation of electron-holes pairs [13]. However, it has a high photogenerated electron-hole pair recombination rate and a limited visible light absorption capacity. Only hydrogen derived from water may be considered an ecologically beneficial energy carrier among these basic sources. When hydrogen is created from water and then burnt, it produces no CO$_2$ [14, 15]. TiO$_2$ has been modified with transition-metal cations to increase its absorption capacity for light hence its photocatalytic capabilities [16, 17]. Several studies have suggested adding chromium oxide to titanium oxide to improve the effectiveness of photocatalysis [18]. Cr$_2$O$_3$ has generally been considered a good photocatalytic material for ultraviolet light because of its tight bandgap, and thus, it has been considered as a TiO$_2$ dopant [17, 19]. Cr$^{3+}$ was mixed with TiO$_2$ powder to increase its photocatalytic capabilities [20]. In this study, animal extract (chitosan) was used to synthesize Cr$_2$O$_3$-TiO$_2$ using impregnation technique. It is possible to detect some of the most important constituents in the animal extract (chitosan), includes basic totals found in the rutin (Rutin is a quercetin rutinoside with glucose and rhamnose sugar groups replacing the hydroxy group at position C-3) vitamin C, and cellulose are also included in chitosan, which are significant components of the chitosan extract [21]. To reduce Cr(NO$_3$)$_3$ hydroxide, chitosan extract partially reduces Cr(NO$_3$)$_3$ hydroxide to generate Cr$_2$O$_3$-TiO$_2$ nanocomposite. The objectives of this work are to synthesise Cr$_2$O$_3$-TNFs nanocomposite and improve photogenerated electron–hole pair efficiency and photocatalytic activity by improving optical responsiveness in ultraviolet range.

2. Experimental work

2.1. Synthesis of TiO$_2$ nanofibers

Commercial TiO$_2$ nanoparticles (from Sky spring Nanomaterial, Inc.) were used as the starting point for the fabrication of TiO$_2$ nanofibers. The hydrothermal technique was used to synthesize TiO$_2$ utilizing both hydrochloric acid (HCl) and sodium hydroxide (NaOH) [10]. First, 3 g of TiO$_2$ was dispersed with ultrasonic-assistance in 100 ml of NaOH (10 M) for 30 minutes, with stirring for 4 hrs. After that, the suspension was placed in a Teflon-lined autoclave container and incubated at 180 °C. The reaction duration was 8 hrs for hydrothermal treatment. The final product was treated with 1.5 ml of HCl overnight and then washed with deionized water until the pH reached 7. After that, the material was filtered and dried at 60°C.

2.2. Preparation of the animal extract (chitosan)

0.5 g of chitosan was dissolved in acetic acid in the water of 1:50 ratio and mixed with the ultrasonic tool for 2 hrs, then filtered using micro porous membrane (pore size0.22μm). The solution was centrifuged at 4000 rpm for 5 minutes to remove any residual salts and impurities.

2.3. Preparation of the Cr$_2$O$_3$-TiO$_2$ nanocomposites using animal extract (chitosan)

Cr$_2$O$_3$-TNFs nanocomposite was synthesized using 0.0329 g of Cr(NO$_3$)$_3$.9H$_2$O with 2 ml anhydrous ethanol solution and 1ml of chitosan extract treated to produce a clear dark blue solution that was then impregnated with 2.5 g of (TNFs). The impregnate was volatilized at 70°C until being annealed for 2 hrs at 300°C.
2.4. Characterization of Cr$_2$O$_3$-TiO$_2$ nanocomposites

Cr$_2$O$_3$-TiO$_2$ nanocomposites were characterized with UV-Visible spectrometer type (DU-8800D-China) within the wavelength range (190-1100) nm and with X-ray diffractometer (SHIMADZU, XRD - 6000, JAPAN) using CuKα radiation ($\lambda=1.5406$ Å). While the morphological properties of Cr$_2$O$_3$-TiO$_2$ nanocomposites were studied with a Field Emission Scanning Electron Microscope (FESEM INSPECT F-50, Company FEI, Dutch) and with energy dispersive (X-Ray) spectroscopy (EDX).

2.5. The assessment of photocatalytic hydrogen generation

As shown in Fig.1, the laboratory cell that was used to separate hydrogen from the water was made locally from quartz glass (6 cm x 28 cm) and consisted of a hydrogen gas cylinder. The cylinder is equipped with holes for the exit of gas; water decomposition was carried out using an analytical system, such that the quantity of photocatalyst measured was 2 g from the Cr$_2$O$_3$-TiO$_2$ placed in a quartz flask containing 500 ml of water and 0.028 M KOH of a sacrificial reagent aqueous solution (Cr$_2$O$_3$-TiO$_2$), which was exposed to ultraviolet light irradiation ($\lambda<$400 nm).

![Figure 1: The local fuel cell used to generate hydrogen from water.](image)

3. Results and discussion

3.1. XRD analysis of TNFs and Cr$_2$O$_3$-TNFs nanocomposite

The XRD pattern of TNFs revealed the planes (101), (103), (004), (112), (200), (105), (211), (204), and (116) with 2θ values of (25.2°), (36.9°), (37.8°), (38.0°), (48.4°), (53.7°), (55.2°), (62.6°), and (68.5°), respectively, as shown in Fig.2. The diffraction peaks revealed a tetragonal anatase phase, according to (JCPDS No.84-1285). The strongest diffraction peak at (25.2°) indicated (101) plane of anatase TiO$_2$ of two patterns, anatase structure by the peaks other than (53.7°), and (55.2°), and rutile structure indicated by the peaks 53.7° and 55.2°. This suggests that the 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 align with the previous research project by Ahmad et al. [20]. The TNFs, average crystallite size, as found by Scherrer's formula [22], was equal to 6.3 nm.
Fig. 3 illustrates the XRD pattern of Cr$_2$O$_3$-TNFs nanocomposite heterostructures at different Cr$_2$O$_3$ percentages. The diffraction planes (101), (103), (004), (112), (200), (105), (211), (204), and (116) (JCPDS Card No. 84-1285), corresponding to $2\theta$ = (24.9°), (36.6°), (37.75°), (38.1°), (48.2°), (53.9°), (55.4°), (62.7°) and (68.5°), respectively, are seen in the crystallized anatase phase of Cr$_2$O$_3$-TNFs. Because of the small proportions of Cr$_2$O$_3$ nanoparticles relative to the TiO$_2$, the XRD patterns showed peaks of Cr$_2$O$_3$ at $2\theta$ = (33.3°), and (44.6°) (JCPDS No. 1308-38-9). According to these findings, the successful modification of titanium dioxide by the addition of Cr$_2$O$_3$ has created flaws in the anatase crystal to form Ti-O-Cr bonds which allowed it to interact with both Cr$^{3+}$ ions and TiO$_2$ [23]. As a result, it was concluded that the presence of Cr$_2$O$_3$ blocked the pore wall of TiO$_2$. The crystal size of Cr$_2$O$_3$-TNF was 12.3 nm. These results showed that the crystal size of TiO$_2$ increased when loaded with Cr$_2$O$_3$.

3.2. FE-SEM images of TNFs and Cr$_2$O$_3$-TNFs nanocomposites with chitosanextract

The morphology of TNFs, as seen from the FESEM images Fig.(4-A) appears as fibers with few rods and a few aggregations. The average particle size appeared to be between 9 and 35 nm (measured using Image J software). Fig.(4-B) shows Cr$_2$O$_3$ with TNFs (rod shapes) nanocomposites. The bonding of chromium and titanium oxide...
particles by weak forces leads to the agglomeration of the nanoparticles and the formation of a large surface area [23].

3.3. EDX of of TNFs and Cr₂O₃-TNFs nanocomposites

EDX analyses of TNPs and Cr₂O₃ with TNFs nanocomposite are shown in Figs. 5 and Tables 1. It reveals the characteristic emission peaks for Ti, O₂ and Cr, in addition to peaks related to C and to some trace elements observed in both samples as a residual from the extracted material, which may be associated with the presence of phytomolecules (polyphenols, alkaloids, and flavonoids) of chitosan extracts adsorbed on TNFs surface.

<table>
<thead>
<tr>
<th>Element</th>
<th>TNFs</th>
<th>Cr₂O₃-TNFs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atomic %</td>
<td>Weight %</td>
</tr>
<tr>
<td>O</td>
<td>51.0</td>
<td>75.7</td>
</tr>
<tr>
<td>Ti</td>
<td>49.0</td>
<td>24.3</td>
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<tr>
<td>Cr</td>
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<td>N</td>
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<td>C</td>
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Fig. 6 depicts the UV-Visible absorption spectra of samples where the TNFs samples exhibit an absorption edge at 310 nm. The energy gap was calculated using the Tauc formula, which was equal to 3.9 eV for TNFs, as shown in Fig. 7. Fig. 8 shows that loading TNFs with Cr\(^{3+}\) improved their absorption in the ultraviolet region. The absorption bands for Cr\(_2\)O\(_3\)-TNFs were around 409 nm; the energy gap of Cr\(_2\)O\(_3\)-TNFs was 2.4 eV, as shown in Fig. 9. The absorption edge of the Cr\(_2\)O\(_3\)-TNFs nanocomposite with chitosan extract shifted to higher wavelength in the visible region as compared to that of the pure TNFs. It may be concluded that proper Cr doping resulted in the narrowing of the anatase TiO\(_2\) band gap. The introduction of dopant levels is the cause of the narrower bandgap. This would also cause an electron to be excited from the valence band to the dopant levels. Cr doping may also act as an electron-capture trap, preventing recombination of electron-hole pairs. Cr doping, on the other hand, produces deep dopant levels, and recombination sites that can speed up the recombination of electron-hole pairs. These results agree with those of Zhu et al. [24].

![Figure 6: Ultraviolet-Visible absorption spectra of the TNFs.](image6)

![Figure 7: The energy gap of (TNFs).](image7)
3.4. Activity of hydrogen production

The photocatalytic decomposition of water under ultraviolet irradiation for different times (10-80) min generated hydrogen from Cr$_2$O$_3$-TNFs nanocomposite as shown in Fig.10. The activity of the Cr$_2$O$_3$-TNFs photocatalyst increased with increasing exposure time (Table 2). The Cr$_2$O$_3$-TNFs photocatalyst has the highest H$_2$ production (4.1 ml) was at (80 min) while the low H$_2$ production (0.4ml) at (20min). It is noted that hydrogen is not produced after 10 min of reaction time. 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. The production of hydrogen gas is twice the production of oxygen gas during the photocatalytic process due to the effectiveness of the reaction of Cr$_2$O$_3$-TNFs nanocomposite.
3.5. The mechanism of photocatalytic hydrogen generation using Cr$_2$O$_3$-TNFs nanocomposite.

Fig. 11 illustrates the mechanism for the photocatalytic decomposition of water to produce hydrogen using Cr$_2$O$_3$-TNFs nanocomposite. The photogenerated electron (e-) moving from Cr$^{3+}$ ions donor level to the conduction band of TNFs, absorbs energy from an ultraviolet photon as described in Eq.(1). Photogenerated electrons move from TNFs' conduction band (CB) to their surface, where they reduce H$_2$O molecules to form H$_2$ and OH$^-$ ions, as in Eq.(2). Meanwhile, photogenerated holes transferred from TNFs' valence band (VB) to the donor level Cr$^{3+}$ which oxidize by H$_2$O molecules, yielding O$_2$ and H$^+$ ions, as illustrated in Eq. (3). It gives more stability to the reaction and the reducing agent for Cr$^{3+}$ ions. The addition of an optimal quantity of Cr$^{3+}$ ions species to the surface of TNFs may lower the recombination rate of photogenerated electron–hole pairs by increasing their separation efficiency, and boosting photocatalytic activity [25].

$$\text{Cr}^{3+} + \text{hv} \rightarrow \text{e}^- + \text{h}^+ \quad (1)$$

$$\text{H}_2\text{O} + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2 + \text{OH}^- \quad (2)$$
\[
\text{H}_2\text{O} + h^+ \rightarrow \frac{1}{2}\text{O}_2 + 2H^+
\]  

(3)

Figure 11: Photocatalytic hydrogen generation mechanism.

4. Conclusions

Hydrothermal and ultrasonic processes were used to create a variety of Cr\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} nanocomposites. An XRD and FESEM analysis of prepared nanocomposites showed that they contained a mixture of Cr\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} (nanofibers). The average diameter of nanofibers was (9-35) nm. The absorption edges of TNFs were extended to visible light region by doping with Cr\textsubscript{2}O\textsubscript{3}. The energy gap was equal to 3.9 eV, which is larger than the energy gap of Cr\textsubscript{2}O\textsubscript{3}-TNFs 2.4 eV because of the appropriate Cr doping that resulted in the narrowing of the band gap of the anatase TNFs. Briefly, it has succeeded in synthesizing environmentally friendly biomolecules via ultrasonic and hydrothermal methods. If the effect of the morphology of the compound Cr\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} was in the form of nanofibers, it was discovered to have an effect on the performance of the current work, where the compound showed a distinguished performance in hydrogen production through photocatalysts (4.1 ml) at 80 min. It can be concluded from this work that nanofibers with a large surface area have the ability to make hydrogen; this is largely dependent on the amount of Cr\textsuperscript{3+} that can be added to the TNFs.

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Conflict of interest

Authors declare that they have no conflict of interest.

References


إضافة إلى ذلك، أظهر المركب النانوي نسبة إنتاج عالية تحت التشعيع الفوق البنفسجي ذات الطول الموجي الأقل يمتلك فعالية عالية للتحفيز الضوئي الناتج من قدرة Cr₂O₃-TNFs من 400 nm. إن المركب النانوي TNFs الامتصاص العالية للضوء الفوق البنفسجي والفصل الممتاز لزوج الإلكترون – فجوة.