

Simultaneous Hydrogen Production with the Degradation of Naphthalene in Seawater Using Solar Light-Responsive Carbon-Modified (CM)-n-TiO₂ Photocatalyst

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ABSTRACT

The simultaneous photocatalytic production of hydrogen and degradation of naphthalene in seawater was successfully achieved using carbon modified titanium oxide (CM-n-TiO₂) nanoparticles under natural sunlight illumination. Compared to unmodified titanium oxide (n-TiO₂), CM-n-TiO₂ nanoparticles exhibited significantly higher photocatalytic efficiency. It is considered that carbon modification is responsible for the significant enhancement in the observed photoactivity. The experimental results indicated that the simultaneous production of hydrogen and degradation of naphthalene was favorable at pH 8 and optimal catalyst dose of 1.0 g·L⁻¹. The solar photocatalytic degradation of naphthalene in seawater using CM-n-TiO₂ successfully fitted using Langmuir-Hinshelwood model, and can be described by pseudo-first order kinetic model.

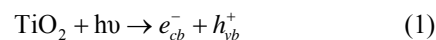
Keywords: Photocatalysis; Titanium Oxide; Carbon Modification; Hydrogen Production; Naphthalene

1. Introduction

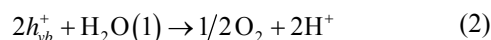
Photocatalysis on semiconductor surfaces has attracted considerable attention in recent years as a potential means for water splitting to produce hydrogen [1-8], and mineralization of organic pollutants present in water and wastewater [9-18]. Among many semiconductor oxides, titanium dioxide (n-TiO₂) has been proven to be the most promising semiconductor due to its optical and electronic properties, low cost, high level of photocatalytic activity, chemical stability and non-toxicity. However, its utilization in the solar light is hampered by the fact that it is a UV absorber. Its wide band gap (3.0 - 3.2 eV) limits its photoresponse in the ultraviolet region which is only a small fraction (~5%). Therefore, several attempts were made to extend its optical response to the visible spectral range by doping with transition metal [19,20], nitrogen [21,22], and sulfur [23]. Recently, it has been reported that carbon modification of n-TiO₂ lowered its bandgap energy to 2.32 eV, and thereby exhibited higher photoresponse [3].

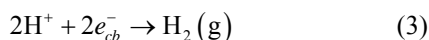
The principle of photocatalysis on titanium dioxide semiconductor is based on the conversion of photon energy to chemical energy. The elementary mechanism of

this process includes a number of steps, which have been exhaustively described in the literature [24,25]. Illumination of TiO₂ by light with energy (hν) greater than or equal to the bandgap energy (E_g) of TiO₂ elevates electron in the valence band (VB) to the conduction band (CB), and a positive hole is formed in the valence band (Equation (1)). The conduction band electron (e_{cb}⁻) is strongly reducing, and the valence band hole (h_{vb}⁺) is strongly oxidizing. At the external TiO₂ surface, the positive hole and the excited electron can take part in redox reactions with adsorbed groups.

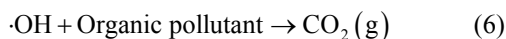
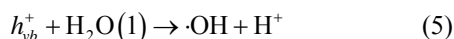
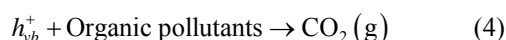


The photoinduced production of hydrogen from water is attained by photogenerated electrons (e_{cb}⁻), provided that their energy is sufficient to reduce protons toward hydrogen molecules (Equation (3)). To achieve this process, the CB level should be more negative than hydrogen production level (E_{H₂/H₂O}) while the VB should be more positive than water oxidation level (E_{O₂/H₂O}) for efficient oxygen production from water by photocatalysis.





One of the major disadvantages of semiconductor photocatalytic system is that, the photo-generated electrons and holes can recombine in bulk or on surface of the semiconductor within a very short time, resulting in reduction in the photocatalytic efficiency. To resolve this problem, electron donors (sacrificial reagents or hole scavengers) were added to react irreversibly with the photogenerated VB holes (h_{vb}^+), thereby suppressing the electron-hole recombination [26,27]. If this sacrificial agent is a pollutant present in water or wastewater, the positive hole (h_{vb}^+) would oxidize either pollutant directly (Equation (4)) or water to produce OH radical (Equation (5)). Consequently, enhancement of the H_2 production rate with simultaneous degradation of the organic substrate can be obtained. A simplified diagram illustrating the simultaneous photocatalytic production of hydrogen and degradation of organic compound using TiO_2 under illumination of light is presented in **Figure 1**.



The vast majority of researches on TiO_2 photocatalysis have focused on a single process; either the photodegradation of pollutants or hydrogen generation under illumination of artificial UV light or simulated sunlight. Despite the importance of seawater as it has been considered to supplement the limited sources of water available for drinking, as well as for the production of hydrogen energy [28], most of the studies on photocatalytic hydrogen production and degradation of pollutants have been performed using pure water. Based on the previous considerations, the present study focused on the synthesis of visible light active carbon-modified (CM)- $n\text{-TiO}_2$ nanoparticles that is capable of harvesting the maximum solar light in the visible region. The simultaneous production of hydrogen and degradation of naphthalene, as a

sacrificial agent, in natural seawater was investigated using the synthesized photocatalyst under illumination of real sunlight. The effects of photocatalyst loading, naphthalene concentration, and pH on the photocatalytic performance were also studied.

2. Experimental

2.1. Synthesis and Characterization of $n\text{-TiO}_2$ and CM- $n\text{-TiO}_2$ Nanoparticles

Regular (unmodified) titanium dioxide ($n\text{-TiO}_2$) nanoparticles were synthesized by hydrolysis and oxidation of titanium trichloride (TiCl_3 12% in hydrochloric acid (5% - 12%), Sigma-Aldrich) in an aqueous medium. Visible light active carbon modified titanium dioxide (CM- $n\text{-TiO}_2$) nanoparticles were synthesized by a sol-gel method using titanium butoxide ($\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$, Fluka, 97%), a carbon-containing precursor, as a molecular precursor of TiO_2 as well as a carbon source. Details on the procedures used for catalysts preparation and characterization can be found elsewhere [18].

2.2. Photocatalytic Experiments

All solar photocatalytic experiments were carried out at the Faculty of Marine sciences, Obhur, Jeddah, KSA, in the daytime between 11:00 am to 15:00 pm, during May-June, 2013. Natural seawater samples were collected from Sharm Obhur, Jeddah, KSA. Before spiking with different concentrations of naphthalene, seawater samples were passed through Whatman GFC to remove any solid particles. Experimental set up consisted of a magnetically stirred 500 mL top-covered Pyrex glass photo-reactor loaded with the seawater solution containing different concentrations of naphthalene ranging from 5 to 20 ppm, then the synthesized photocatalyst ($n\text{-TiO}_2$ or CM- $n\text{-TiO}_2$) was added. Prior to the reaction, the mixture was purged with N_2 gas (99.999%) to remove any atmospheric oxygen. The photocatalytic reactor was then directly exposed to natural sunlight. The average solar intensity was about $1200 \text{ W}\cdot\text{m}^{-2}$, measured by Field Scout Light Sensor Reader (Spectrum Technologies, Inc.) equipped with 3670i Silicon Pyranometer Sensor. The amount of photogenerated hydrogen was analyzed using a gas chromatograph (Bruker, GC-450), equipped with a thermal conductivity detector (TCD), high purity Ar (99.999%) was used as a carrier gas. Analysis of naphthalene content in solution has been achieved with the use of a Shimadzu UV-VIS Spectrophotometer (Model PharmaSpec UV-1700). Prior to analysis, aliquots of treated seawater samples were regularly withdrawn from the reactor and centrifuged immediately to remove the catalyst. The supernatant was then immediately analyzed for its naphthalene content. The photodegradation efficiency (η) was calculated from the decrease of the absorbance of naph-

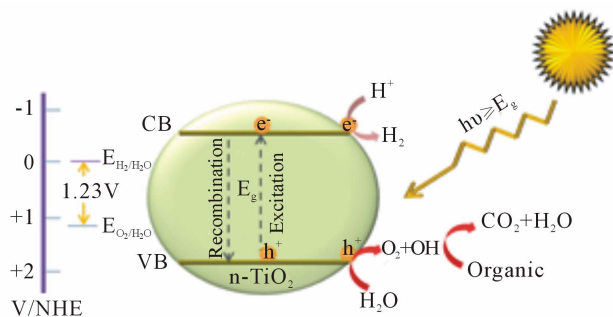


Figure 1. A simplified diagram of the simultaneous photocatalytic production of hydrogen and degradation of organic compound using TiO_2 under illumination of light.

thalene at its maximum absorption wavelength (275 nm) as follows:

$$\eta = \left[\frac{C_0 - C_t}{C_0} \right] \times 100 \quad (7)$$

where C_0 represents the initial concentration of the naphthalene and C_t represents the concentration of naphthalene at solar light irradiation time (t).

3. Results and Discussion

3.1. Photocatalytic Activity of n-TiO₂ and CM-n-TiO₂

In order to examine the photocatalytic efficiency of CM-n-TiO₂, comparison with unmodified n-TiO₂ was performed under the same experimental conditions. It is clearly observed that the photocatalytic efficiency of CM-n-TiO₂ towards the simultaneous photocatalytic production of hydrogen and degradation of naphthalene (10 ppm) in seawater under illumination of natural sunlight is much higher than that of n-TiO₂ (**Figure 2**). The enhanced photocatalytic activity of carbon modified CM-n-TiO₂ nanoparticles can be attributed to carbon modification of TiO₂ [3,5-8,17,18].

3.2. Effect of Solution pH

It is known that the pH of the solution is a key parameter in the photocatalytic reactions, it can directly influence the surface charge of the semiconductor, thereby affecting the interfacial electron transfer and the photoredox process [29]. The possible functional groups on TiO₂ surface in water are TiOH₂⁺, TiOH, and TiO⁻. The point of zero charge (pH_{pzc}) of TiO₂ is an important factor determining the distribution of the surface groups.

When pH > pH_{pzc}, the surface of TiO₂ is negatively charged with the species TiO⁻ (Equation (8)), and positively charged with the species TiOH₂⁺ at pH < pH_{pzc} (Equation (9)).



The role of pH in the photocatalytic production of H₂ and degradation of naphthalene in seawater under illumination of natural sunlight using CM-n-TiO₂ was studied by keeping all other experimental conditions constant and varying the initial pH of the solution from 3 to 9. As can be seen in **Figure 3**, both the production of H₂ and degradation of naphthalene rapidly increased with increasing the pH from 3 to 8, beyond which the photocatalytic production of H₂ and degradation of naphthalene started to decrease, indicating an optimum pH of approximately 8 for best performance. As the high redox potentials of Equation (3) in acidic condition, the formation of hydroxyl radicals will be thermodynamically un-

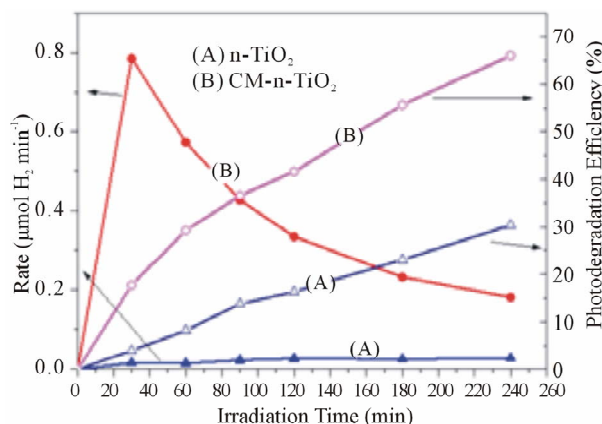


Figure 2. Simultaneous degradation of naphthalene (10 ppm) and production of hydrogen in the presence of n-TiO₂ and CM-n-TiO₂ under illumination of natural sunlight.

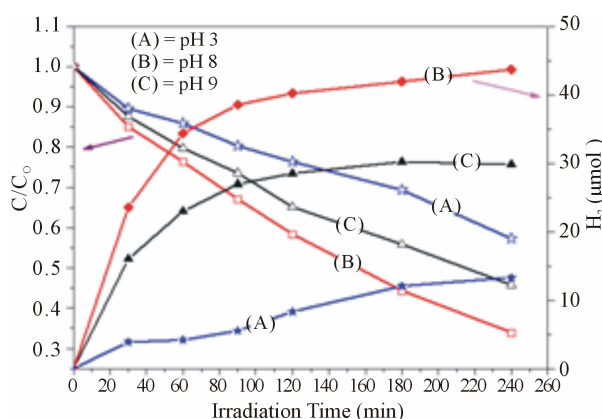


Figure 3. Effect of pH on the simultaneous degradation of naphthalene (10 ppm) and production of hydrogen in the presence of 1.0 g·L⁻¹ of CM-n-TiO₂ under illumination of natural sunlight.

favorable [30]. As a result, the formation of hydroxyl radicals increased with an increase in pH from 3 to 8, resulting in an increased photocatalytic efficiency. At pH higher than 8, the formation of carbonate ions is favorable which are effective scavengers of hydroxyl ions and can reduce the efficiency of photocatalytic process [31, 32].

3.3. Effect of Catalyst Dose

The influence of CM-n-TiO₂ dose on the photocatalytic production of H₂ and degradation of naphthalene (10 ppm) in seawater under illumination of sunlight was investigated at the optimal pH value (pH 8) to ensure maximum absorption of efficient solar light photons as well as to avoid an ineffective excess amount of catalyst (**Figure 4**).

Both the photocatalytic degradation rate of naphthalene and the production of H₂ increased with the increase in catalyst dose from 0.5 to 1.0 g·L⁻¹. The increase in

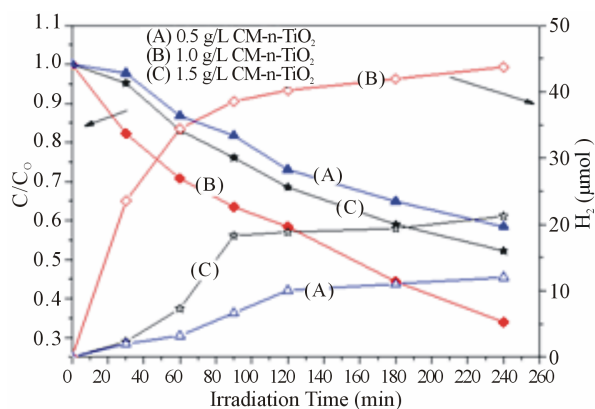


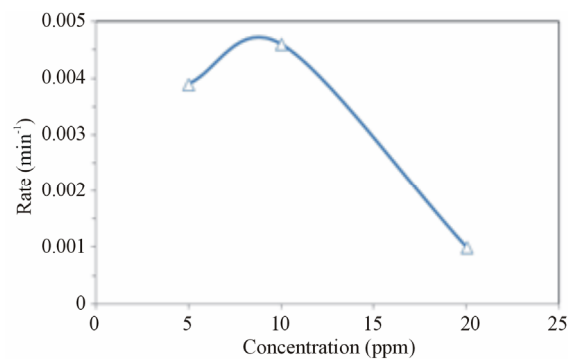
Figure 4. Effect of CM-n-TiO₂ dose on the simultaneous degradation of naphthalene (10 ppm) and production of hydrogen under illumination of natural sunlight.

catalyst amount actually increases the number of active sites on the photocatalyst surface thus causing an increase in the number of e_{cb}^- and h_{vb}^+ which can take part in photocatalytic processes. Further increase in the catalyst loading to $1.5 \text{ g}\cdot\text{L}^{-1}$ slightly decreased the photocatalytic efficiency. At catalyst loading beyond the optimum, the tendency toward particles aggregation increases, resulting in a reduction in surface area available for light absorption and hence a drop in photocatalytic degradation rate [33]. Additionally, the increase of the turbidity of the suspension reduces light penetration due to the enhancement of light scattering; the result is the decrease of the number of activated sites on the TiO₂ surface and shrinking of the effective photoactivated volume of suspension. The interplay of these two processes resulted in a reduced performance of photocatalytic activity with the overloaded catalyst [34,35]. In this study, the dosage of $1.0 \text{ g}\cdot\text{L}^{-1}$ of CM-n-TiO₂ can be considered as the optimal catalyst loading.

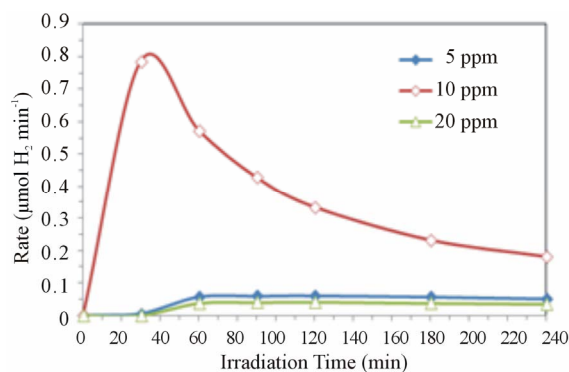
3.4. Effect of Initial Naphthalene Concentration

The initial concentration of naphthalene is an important factor which needs to be taken into account. The effect of the initial naphthalene concentration on its photodegradation rate and the photocatalytic production of H₂ was investigated over the range of 5 to 20 ppm at the optimal conditions of pH 8 and $1.0 \text{ g}\cdot\text{L}^{-1}$ of CM-n-TiO₂ (Figure 5). Both the photoinduced production of H₂ (Figure 5(a)) and degradation rate of naphthalene (Figure 5(b)) rapidly increased with the increase in naphthalene concentration from 5 to 10 ppm. Further increase of naphthalene concentration to 20 ppm, resulted in a remarkable decrease in the rate of degradation of naphthalene as well as the production of H₂.

This can be explained by the saturation of the limited number of accessible active sites on the photocatalyst surface and/or deactivation of the active sites of the catalyst. Several studies have reported that high organic



(a)



(b)

Figure 5. (a) Rate of photodegradation of naphthalene as a function of naphthalene concentration at the optimal conditions of pH 8 and $1.0 \text{ g}\cdot\text{L}^{-1}$ of CM-n-TiO₂; (b) Rate of hydrogen evolution as a function of solar irradiation time at the optimal conditions of pH 8 and $1.0 \text{ g}\cdot\text{L}^{-1}$ of CM-n-TiO₂ in the presence of 5, 10, and 20 ppm of naphthalene.

substrate loadings induce the formation of intermediates that could be adsorbed onto the catalyst surface and deactivate the active sites [36,37].

3.5. Kinetics of Photodegradation

To study the kinetics of photocatalytic degradation of naphthalene in seawater using CM-n-TiO₂, Langmuir-Hinshelwood (L-H) model was applied. L-H model basically relates the degradation rate (r) and reactant concentration in water at time t (C), which is expressed as follows:

$$r = -\frac{dc}{dt} = \frac{k_r K_{ad}}{1 + K_{ad} C} \quad (10)$$

where k_r is the rate constant and K_{ad} is the adsorption equilibrium constant [38-41]. When the adsorption is relatively weak and/or the reactant concentration is low, equation (10) can be simplified to the pseudo-first order kinetics with an apparent first-order rate constant k_{app} :

$$\ln\left(\frac{C_o}{C}\right) = k_r K_{ad} t = k_{app} t \quad (11)$$

where C_o is the initial concentration. Figure 6 shows the plot of $\ln(C_o/C)$ versus illumination time for the

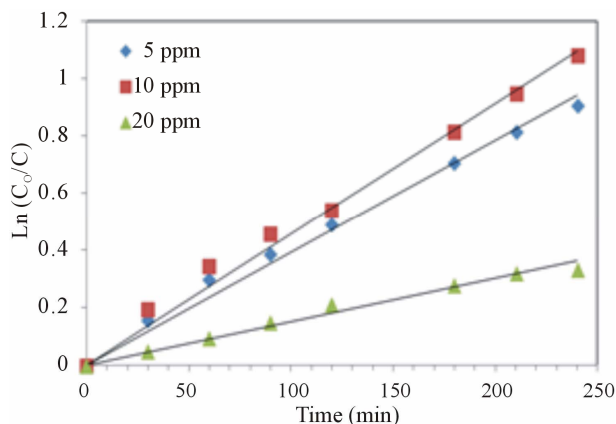


Figure 6. Plot of $\ln(C_0/C)$ versus illumination time for the photocatalytic degradation of naphthalene (5 - 20 ppm) in seawater under natural sunlight illumination using $1.0 \text{ g}\cdot\text{L}^{-1}$ CM-n-TiO₂.

photocatalytic degradation of naphthalene (5 - 20 ppm) in seawater under natural sunlight illumination at the optimal conditions of pH 8 and $1.0 \text{ g}\cdot\text{L}^{-1}$ of CM-n-TiO₂. The linearity of the plot confirmed that the photocatalytic degradation of naphthalene using CM-n-TiO₂ follows the L-H model, and can be described by pseudo-first order kinetics.

4. Conclusion

The photocatalytic production of hydrogen accompanied by the simultaneous degradation of naphthalene in seawater was successfully achieved using carbon-modified (CM)-n-TiO₂ nanoparticles under irradiation of natural sunlight. CM-n-TiO₂ nanoparticles exhibited significantly enhanced photocatalytic efficiency compared to unmodified n-TiO₂. This observed enhancement in the photoactivity can be attributed to the carbon modification. The simultaneous production of hydrogen and degradation of naphthalene was favorable at pH 8 and optimal catalyst dose of $1.0 \text{ g}\cdot\text{L}^{-1}$. The solar photocatalytic degradation of naphthalene in seawater using CM-n-TiO₂ successfully fitted using Langmuir-Hinshelwood model, and can be described by pseudo-first order kinetic model.

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