



HYDROGEN GAS PRODUCTION FROM WASTEWATER BY TiO₂ AND NITROGEN-DOPED TiO₂ NANO FIBERS WITH SIMULTANEOUS POLLUTANTS REMOVAL

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ABSTRACT

At this work we synthesized electrospun titanium oxide (TiO₂) and nitrogen-doped titanium oxide (N-doped TiO₂) for producing hydrogen (H₂) in the same time pollutant removal from wastewater by photocatalytic oxidation at room conditions. We used titanium isopropoxide (TiP)/polyvinylpyrrolidone (PVP) solution to prepare dispersed titanium oxide in polymer nanofibers by sol-gel processing and electrospinning techniques. TiO₂ is a very effective and brilliant photocatalyst for water treatment, but it has drawbacks like absorbing UV light and fast backward reaction and recombination between electrons and generated holes pairs, there are much effort has been devoted to overcome its problems, like doping with metals and non-metals. Advantage of N-doped TiO₂ nano fiber is expanded the utilization of a large part of the solar spectrum. This might be useful for environmental and energy applications, such as the photocatalytic degradation of organic pollutants, solar cells, sensors, and water splitting reactions. The photocatalytic activity of TiO₂ and N-doped TiO₂ nanofibers was carried out in the waste and dye water-splitting reaction to produce H₂ and water treatment using mercury light irradiation. The doping of TiO₂ with Nitrogen, which should improve the electronic properties, leading to activation as a photocatalyst under visible light irradiation. Several characterization techniques are employed for studying the surface morphology, phase of structure, and binding energy for TiO₂ and N-TiO₂ nanofibers (Scanning electron microscopy, X-ray diffractometry, transmission electron microscope).

Keywords: Photocatalysis; wastewater treatment; H₂ production; Electrospinning synthesis of TiO₂ and N-doped TiO₂ nano fiber

INTRODUCTION

Photo-catalysis is defined as "acceleration of the photo-reactions rates by employing of the photo-catalysts, it can convert solar energy to chemical energy upon a metal oxide nanostructure. Also photo-catalyst coupled with light can split water into two main components (oxygen and hydrogen) to produce H₂ fuel to be used as a clean renewable energy. So we consider that photo-catalysis as a promising, environmentally friendly process [1]. Metal oxide nanostructures, such as TiO₂, ZnO, and SnO₂, have great impact in the photo-catalytic oxidation of organic pollutants. Between several elects for photo-catalysts, titanium oxide (TiO₂)

is the most material suitable for industrial application. This is because TiO₂ has the most efficient photo-activity, the highest chemical and physical stability under the reaction conditions, its optical and electronic properties, non-toxicity and the lowest cost. As a reason of TiO₂ wide band gap (band gap=3.2 eV), it is effective under ultraviolet irradiation [2-6]. To overcome this problem by enhancing the performance of TiO₂ to absorb visible region solar light, many techniques such as sensitizing TiO₂ with dye and doping the TiO₂ with metal and non-metal element have been developed [7, 8].

Doping TiO₂ by nitrogen (N) atoms has been studied on a large scale and N alteration in TiO₂ is useful for narrowing the energy band gap efficiently and

increasing the solar light wavelength range [9-10]. Publication by Asahi et al. in 2001 leads to rapid growth of research in this area which discussed that N- doping of TiO₂ gives an effective narrowing of the band gap to the value corresponding to the visible light photon energy, as a result of the overlap of the 2p states of oxygen and nitrogen [11].

We can fabricate N-doped TiO₂ in different forms such as nanotube, nanoparticle, nanorod, nanosheet, and nanofiber. In our study, we choose nanofiber form for fabrication by electro-spin process because of long-continuous fiber, stripped its diameter size, porous structure after calcination and simple process. Electro-spinning is a developed technique that produces continuous nanofibers from polymer solutions using electrical forces [12, 13]. This process help to treatment physical properties of the polymer such as diameter, porosity, interconnectivity, orientation and compositions [13, 14]. Metal nanoparticles combined to electro-spun fiber can be used as highly sensitive electrodes [15, 16], proton exchange membrane [17] and catalytic layers [18].

1.1 Principle of Electro-spinning.

There are three principle components to complete a functional electro-spinning set-up: a high voltage power supply, a needle of small diameter, and a grounded metal collecting screen. A small amount of the fluid pumped out over the syringe needle leads to form a spherical droplet. When the applied voltage is sufficiently high, the electric field force beats the surface tension and, if the molecular cohesion of the liquid is sufficiently high, a stable charged liquid jet is ejected from the apex of the cone. The jet continues to decrease in diameter until it starts to bend and enters an instability regime. As a result, it undergoes a continuous elongating-and-whipping process leading to the formation of a long and thin thread that finally deposits onto the collector. Since the solvent almost completely

evaporates during the motion of the jet towards the collector, a non-woven mat of solid fibers is obtained by this process [19-23].

1.2 Photo-catalytic activity of doped - TiO₂

Doping technique can improve the activity of photo-catalyst and overcome limitations of nano TiO₂ such as wide band gap, ineffectiveness of photo-catalysis under the sunlight and thermal instability [24, 25]. Dopants can adjust the electronic structure of nano TiO₂ for more useful of light region [26]. Another advantage of dopants is the ability to give good physicochemical properties such as high specific surface area, high crystallinity (high percentage of anatase phase), and small crystallite size. [27-29]. In addition to the ability of dopants to create a charge space on the surface of TiO₂ and delete the electron-hole recombination, dopants play a role as active site for the adsorption of pollutants and improve the rate of photo-degradation [30].

1.3 Photo-catalytic activity of non-metal doped TiO₂ nanofibers.

Substitution of O by N is difficult because of the difference of the ionic radius between N (1.71 Å) and O (1.4 Å). Thus, to preserve the electro-neutrality and to form an oxygen vacancy, three oxygen atoms have to be replaced by two nitrogen atoms. In the presence of nitrogen in Titania, the energy of oxygen vacancies is reduced from 4.2 to 0.6 eV, cleared that nitrogen favors the formation of oxygen vacancies [31]. As shown in Fig.1., these oxygen vacancies enhance the absorption in the visible region (from 400 to 600 nm) and ensure the activation of N-doped TiO₂.

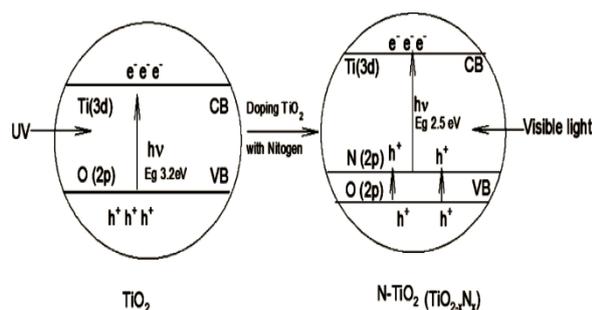


Fig.1. Energy Level of N- doping TiO_2 [32].

2. EXPERIMENTAL

2.1 Materials

1. Titanium isopropoxide (Ti (Iso)) ($\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$) as a precursor for Titanium.
2. Poly vinyl pyrrolidone (PVP, Mw= 130000) ($\text{C}_6\text{H}_9\text{NO}$) as a polymer.
3. Thiourea (Assay 99.9%) ($\text{CH}_4\text{N}_2\text{S}$) as a precursor for nitrogen.
4. Ethanol (Assay 99.8-100%) as a solvent for PVP.
5. Acetic Acid (Assay 99%) to prevent coagulation of Ti(Iso).
6. Waste water "Sewage water" COD=445 mg/l
7. Methylene blue 10.88 p.p.m $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}, 3\text{H}_2\text{O}$, wave length 664 nm.

2.2 Method

The electro spinning process is the method used for nanofiber production.

2.3 Catalyst preparation:

i) PVP solution (TiO_2 without doping) was prepared by:-

- 1) Dissolve the PVP polymer granules (2g) in pure ethanol (12g) to form a final polymer solution having 14.7 wt% concentrations; the mixture was stirred at 30°C until complete solubility.
- 2) Add 4g ethanol to 4g acetic acid and a stirring for 5 min, inject 2 ml titanium isopropoxide in the solution, and let the mix on a quit stirrer for 15min.
- 3) Mix the two solutions to obtain clear solution.
- 4) Electro-spinning process was used to form a sheet of TiO_2 nano-fiber.
- 5) Dry the sheet at 60°C under vacuum.
- 6) Calcinations at 700°C for 5 h.

ii) Preparation of the N-doped TiO_2 Nfs:

- a) Making a stock solution from the PVP: Dissolve 2g of PVP in 12 ml of absolute ethanol.

iii) Preparing of the doped solutions:

1. To make Titanium Isopropoxide ((TTIP) solution: add 2 ml (TTIP) to 4 ml absolute ethanol and 4 ml acetic acid and then stir until the solution becomes homogenous.
 2. For preparing thiourea doping percent as 0.5%, 0.1%, 0.05%, and 0.01%; we take 0.764g, 0.1527g, 0.0764g, and 0.0152g thiourea, respectively and add to it 2 ml ethanol and stir for about 1h and use heater if necessary, to make a clear solution
 - c) Add the stock sol. of the PVP to the desired concentration of thiourea solution, dimethylsulphoxide solution and sodium di-hydrogen orthophosphate solution and then continuous stir for at least 1 h.
- After that preparation of N-doped TiO_2 solution by mixing thiourea as Nitrogen source at 0.01, 0.05, 0.07, 0.1, 0.5 wt.% in 4 mL of ethanol and 4 mL of acetic acid and stirred for half an hour, then injection 2 g of titanium isopropoxide and stirred for 15 minutes. Mix the solution of polymer with

doping solution and metal solution until the solution becomes clear. Then electro-spin the sol. gel with an electro spinning machine at 15KV with a distance between the tip and the rotating cylinder about 20cm. Finally, dry the fiber sheat for 24h at 60°C, then calcinen the product at 700°C for 5 h at a rate of 5°C/min at atmosphere.



Fig.2. Samples after drying for 24 h at 60° C.

3. RESULTS AND DISCUSSION

3.1 Physical characterization

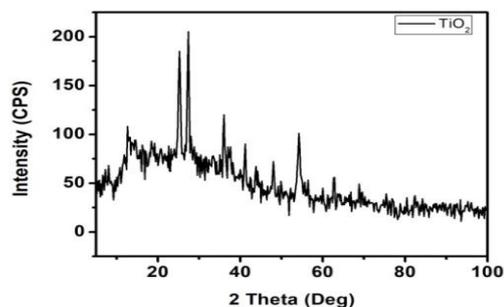
The fabricated fibers were dried under vaccum at 60°C for 24 h, and finally obtained after calcined at 700°C for 5 h. The phase and crystallinity of the catalyst nanofibers were characterized by X-ray diffractometer (XRD); the distribution of metal was characterized by a transmission electron microscope (TEM), and (SEM) analysis.

3.2. Characterization of photo-catalysts (TiO₂ and N-doped TiO₂)

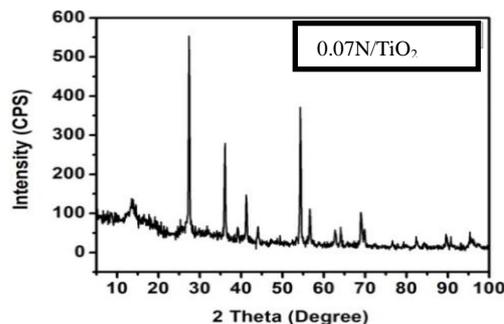
3.2.1 X-ray diffraction studies

XRD is a reliable technique to investigate the nature of any crystalline compounds. It can be seen that the diffraction patterns of all samples are correspond to crystalline, tetragonal anatase TiO₂ phase [33]. Furthermore, no significant patterns related to nitrogen precursors are found in doped TiO₂ nanofibers, due to either proper

substitution of few sites of oxygen by dopant or lower amount of nitrogen in TiO₂ lattice [34]. Structure analysis of the pure TiO₂ (Fig.3. curve a) exhibited characteristic anatase phase pattern (JCPDS 89–4921), with diffraction peaks at 2 theta values of 25.4° (101), 37.8° (004), 48.2° (200), 53.9° (105), 55.2° (211), 62.8° (204), 69.0° (116), 70.5° (200) and 75.2° (215), these results is in good agreement with (41). Diffractograms of N-doped TiO₂ nanocomposites (Fig.3. curve (b)) showed very similar pattern to anatase, without additional peaks. The typical diffraction peaks for N-doped TiO₂ appear at 2 theta values of 21.1, 23.8 and 36° [35–37]. This indicated that no change in crystalline structure was produced during the preparation of these photo-catalysts. On the other hand, even though the diffractograms corresponding to N-doped TiO₂ nano - composites showed similar pattern to pure TiO₂, additional peaks at 21.6 and 24° were observed. These reflection peaks corresponded to a typical orthorhombic unit cell structure of (110) and (200) reflection planes respectively, corresponding to N-doped TiO₂ [38, 39].



(a)



(b)

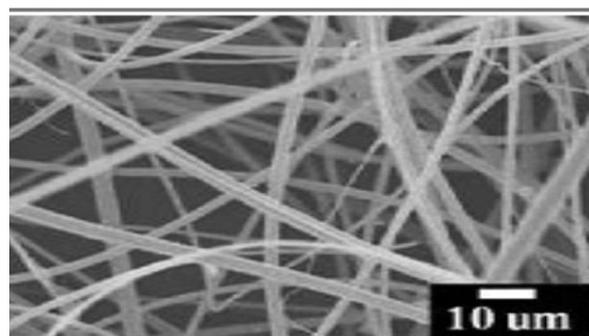
Fig.3. XRD patterns for (a) TiO₂ and (b) 0.07% N- doped TiO₂ nano fibers.

Fig.3. presents the XRD patterns of calcined TiO_2 fibers. It displays sharp and well-defined peaks, indicating the crystallinity of the synthesized materials. This XRD results indicate the formation of TiO_2 with crystalline phase of anatase and rutile without noticeable alternation in phase after nitrogen doping.

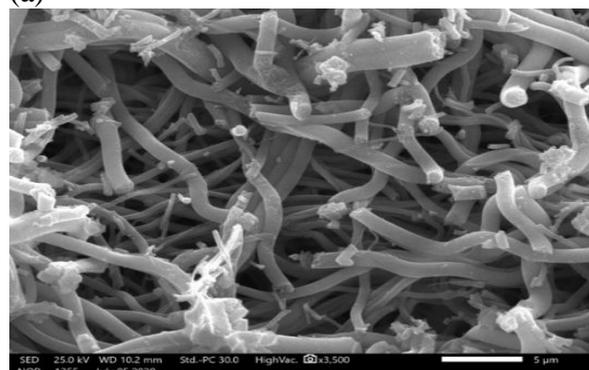
3.2.2 Scanning electron micro-scope (SEM)

SEM images in Fig.4. show the morphologies of as-synthesized and after calcined of un-doped TiO_2 NF. Morphologies of as-synthesized of un-doped exhibit non-uniform nanofibers with beads as observed in Fig.4. (a). Meanwhile, Fig.4.(b) show uniform nanofibers of un-doped and N-doped TiO_2 , continuity and smooth surface caused by burn-out of PVP from the nanofibers after calcinations. After-calcined TiO_2 NFs have average diameter of 140-180 nm. Viscosity was relatively lower than the surface tension at low polymer concentrations. Beads are products of instability of the jet under electric field. It was found that the critical concentration as 10 wt. % of PVP to make fully developed TiO_2 fiber without bead formation. Electrospun TiO_2 /PVP fiber with about 150 nm was prepared from such conditions as the applied voltage of 20 kV and the flow rate of $100\mu\text{l}/\text{min}$ and the TCD of 10 cm. As the calcination time increased, average diameter of TiO_2 nanofibers decreased to about 70 nm up to 4 hr.

Calcined TiO_2 nanofibers at 700°C showed that they consisted of linked polycrystalline structure. The reason may be due to the better crystalline growth with increasing the calcinations temperature.



(a)



(b)

Fig.4. SEM image for TiO_2 nano fiber before doping

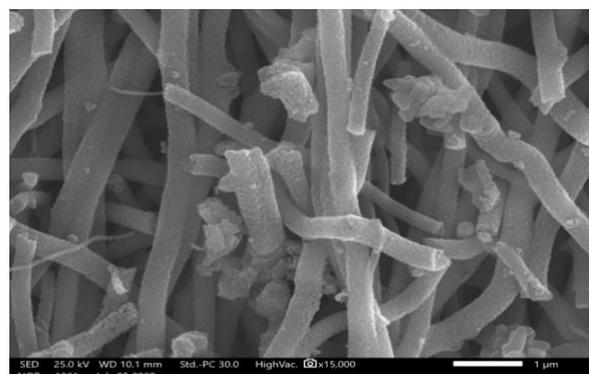
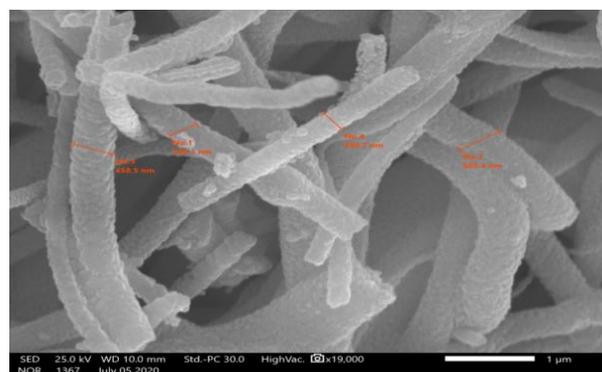


Fig.5. SEM patterns for N- doped TiO_2 nano fibers.



water level every 5 minutes till stop of hydrogen generation

3.3.1 Results of water splitting reaction

i) Photo catalytic hydrogen production from water splitting (waste water case)

Fig.9. illustrates the effect of TiO₂ and TiO₂ doped with different concentration of N on hydrogen evolution from water splitting under the mercury lamp. The results showed high catalytic activity toward hydrogen production from TiO₂-doped with N than TiO₂ under the mercury lamp.

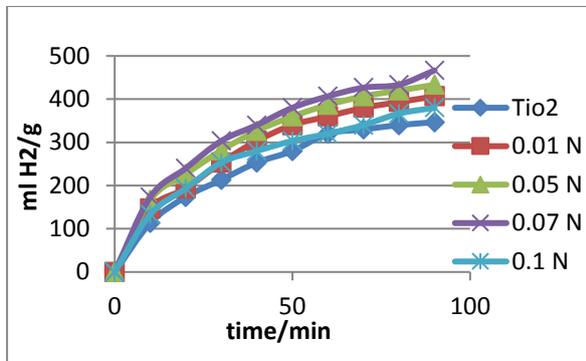


Fig.9.Influence of N content on the hydrogen production at waste water case.

Figure 10 show that doping TiO₂ with N increases the rate of hydrogen production. As TiO₂ gives 346.6 ml hydrogen/g and 0.01, 0.05, 0.07 and 0.1 N -doped TiO₂ give 406.6, 433.3, 466.6 and 380 ml hydrogen/g respectively, and show that doping TiO₂ with N increases the efficiency of hydrogen production until 0.07% percent then start to decrease because of the exhaustion of the catalyst activity.

ii) Photo catalytic hydrogen production from water splitting (methylene blue case)

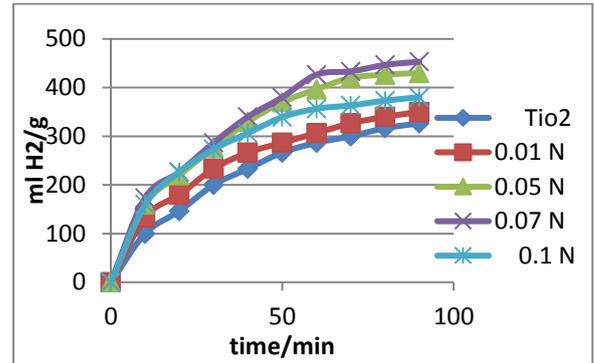


Fig.10.Influence of N content on the hydrogen production (methylene blue) case.

Fig.10. show that doping TiO₂ with N increases the rate of hydrogen production. As TiO₂ gives 326.6 ml hydrogen/g and 0.01, 0.05, 0.07 and 0.1 N -doped TiO₂ give 346.6, 430, 453.3 and 366.6 ml hydrogen/g respectively, and show that doping TiO₂ with N increases the efficiency of hydrogen production until 0.07% percent then start to decrease.

3.3.2. Stability and recyclability of catalysts:

The reusability of photocatalyst was tested for hydrogen production under identical reaction conditions. The catalyst was alienated and washed with a bulky amount of deionized water. The improved catalyst was dried in a hot air oven at 100 °C for 90 min and used for a second run. Figure 14 shows the results of reuse experiments for four runs.

i) Stability and recyclability of catalysts at waste water case:

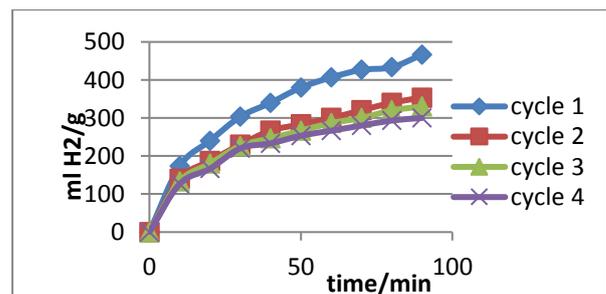


Fig.11. effective reuse of 0.07 N-doped TiO₂ photocatalyst in hydrogen production at waste water case. For four cycles

The reusability of catalyst show high production of hydrogen for four cycles, results 466.6, 353.3, 330, and 300 ml/g respectively, where 466.6 is the fresh use of the catalyst and the efficiency of the three cycles are 75.7, 70.7, 64.3 % respectively. The predicted maximum number of time for reusing the catalyst is about 5 cycles.

ii) Stability and recyclability of catalysts at methylene blue case:

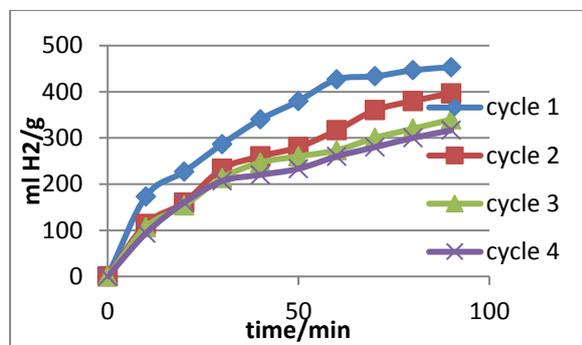


Fig.12. effective reuse of 0.07 N-doped TiO₂ photocatalyst in hydrogen production at methylene blue case for four cycles.

The reusability of catalyst shows high production of hydrogen for four cycles, results are 453.3, 396.6, 330, and 316 ml/g respectively, where 453.3 is the fresh use of the catalyst and the efficiency of the three cycles are 87.5, 72.7, 69.7 % respectively. The predicted maximum number of time for reusing the catalyst is about 5 cycles.

3.3.3 Nano fibers effect on degradation.

i) The effect of Nanofibers on pollutant degradation of wastewater.

The chemical oxygen demand (COD) test is widely used as an effective technique to measure the organic strength of wastewater. The test allows the measurement of waste in terms of the total quantity of oxygen

required for the oxidation of organic matter to CO₂ and water.

The photo catalysis of wastewater has been studied for removal COD and TSS. Maximum COD removal of the wastewater achieved was 77% after catalyst dosage of 0.07 gm% and 57% for TSS at alkaline pH 8 and at ambient temperature. The photocatalytic degradation process using TiO₂ as an irradiation source showed potential application for the COD removal of the sewage.

Initial concentrations are COD= 445mg/l and TSS=140

Table 1 concentrations of waste water after degradation.

Photocatalyst	COD	TSS
Nanofiber TiO ₂	189	117
Nanofiber N-doped TiO ₂	103	60

ii) The effect of Nanofibers on degradation of methylene blue.

Maximum degradation of methelene blue achieved was 61% after catalyst dosage of 0.07 g at ambient temperature and alkaline pH 8; we can control the alkaline of pH by adding NaOH. We can calculate the concentration of the dye by multiplying the obtained absorbance by the dilution factor. Initial Concentration of M.B before traetm=10.88ppm

Table 2 concentration of M.B after degradation.

Photocatalyst	Concentration of M.B.
Nanofiber TiO ₂	6.3 ppm
Nanofiber N-doped TiO ₂	4.22 ppm

4. CONCLUSIONS

- Due to fast electrons/holes recombination, titanium oxide nanocatalyst has relatively low

photo-catalytic activity toward hydrogen production.

- Doping of the titanium oxide nanofibers using some foreign nanoparticles having the ability to collect the excited electrons annihilates the electrons/holes recombination which has positive impact on the photo-catalytic activity of Titania.
- Doping of the titanium oxide nanofibers can be achieved by using the sol-gel process and electro-spinning. Typically, Generally, N-doped TiO₂ nano fibers show a strong improvement in the photo-catalytic activity of the TiO₂ toward both of water photo splitting and dye degradation under visible light radiation.
- The degradation of the organic contaminant, methylene blue, was evaluated with a UV-spectrophotometer. Results showed a steady reduction in methylene blue concentration over time when the immobilized titanium was exposed to mercury lamp irradiation. This degradation was found to perform at a rate much higher than the rate of mercury lamp exposure without titanium present. The study was conducted to evaluate the reduction of COD in distillery wastewater using TiO₂ and N-doped TiO₂ catalyst. From the experiments conducted, it can be seen that photo-catalysis of distillery wastewater was an efficient process of degrading COD.

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إنتاج غاز الهيدروجين من مياه الصرف بواسطة TiO_2 و N-DOPE TiO_2 ألياف النانو بالتزامن مع إزالة الملوثات

الملخص العربي

لقد قمنا بتحضير أكسيد التيتانيوم المغزول كهربائياً (TiO_2) وأكسيد التيتانيوم المشبع بالنيتروجين (N-doped TiO_2) لإنتاج الهيدروجين (H_2) في نفس الوقت إزالة الملوثات من مياه الصرف عن طريق الأكسدة الضوئية في ظروف الغرفة. تم استخدام التيتانيوم ايزو بروبوكسيد (TiP) / محلول بولي فينيل (polyvinylpyrrolidone) PVP لتحضير أكسيد التيتانيوم المغموس في ألياف نانوية بوليمرية عن طريق معالجة سول-جل وتقنيات الغزل الكهربائي. أكسيد التيتانيوم هو محفز ضوئي فعال للغاية ورائع لمعالجة المياه ، ولكن له عيوب مثل امتصاص ضوء الأشعة فوق البنفسجية والتفاعل الخلفي السريع وإعادة التركيب بين الإلكترونات وأزواج الثقوب المتولدة ، هناك الكثير من الجهد الذي تم تكريسه للتغلب على مشاكله ، مثل دمج مع المعادن و غير المعادن. يتم توسيع ميزة الألياف النانوية N-doped TiO_2 باستخدام جزء كبير من الطيف الشمسي. قد يكون هذا مفيداً للتطبيقات البيئية والطاقة ، مثل التحلل التحفيزي للملوثات العضوية ، والخلايا الشمسية ، وأجهزة الاستشعار ، وتفاعلات تقسيم المياه. تم تنفيذ النشاط التحفيزي الضوئي لألياف TiO_2 و TiO_2 النانوية المخدر N في النفايات وصبغة المياه- تفاعل الانقسام لإنتاج H_2 ومعالجة المياه باستخدام ضوء الزئبق. تشريب TiO_2 بالنيتروجين ، والذي يجب أن يحسن الخصائص الإلكترونية ، مما يؤدي إلى التنشيط كمحفز ضوئي تحت إشعاع الضوء المرئي. يتم استخدام العديد من تقنيات التوصيف لدراسة التشكل السطحي ، ومرحلة الهيكل ، وطاقة الربط للألياف النانوية TiO_2 و N-TiO_2 (الفحص المجهر الإلكتروني ، قياس حيود الأشعة السينية ، مجهر الإرسال الإلكتروني).

الكلمات الدالة: TiO_2 N-doped TiO_2 ؛ التحفيز الضوئي؛ تركيب الغزل الكهربائي؛ مياه الصرف الصحي، إنتاج H_2 كفاءة تحويل الضوء نشاط التحفيز الضوئي ؛ الطلب على الأكسجين الكيميائي (COD).