H₂ Production From Wastewaters Containing Sulphur via Photocatalysis Using TiO₂-N-GO Nanocomposite

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Keywords: GO, TiO₂-N-GO, chemical industry, wastewater, H₂S, H₂ production.

Introduction
Among various kinds of energy resources, hydrogen is one of the potential green energy sources because of its eco-friendliness, high energy combustion, and carbon-free emission (Han et al., 2012). Recently, the solar-drivable photocatalytic water-splitting technique has emerged as a prominent way to produce hydrogen from wastewater (Khan et al., 2002). In general, the semiconductive photocatalysts show the outstanding activity of photocatalytic water-splitting; however, the photo-corrosion and the fast photocarrier recombination have restricted their tangible application for photocatalytic hydrogen production (Maeda et al., 2006). To overcome this issue, many types of strategies have been proposed; for example, the incorporation of various dopants into carbon-based materials, noble metals, and non-metals as well as the formation of co-catalysts with homo- and hetero-structures using transition-metal oxides (TMOs) (Zou et al., 2004). To achieve a higher hydrogen-production efficiency, fabricating the high-quality TMO-based semiconductive photocatalysts is essential. Particularly, a higher photo-stability and a higher photo-response to visible light are desired to increase the photocatalytic hydrogen-production efficiency. Considering such criteria, titanium dioxide (TiO₂) can be an excellent candidate for photocatalysts because of its high photo-stability, high conductivity, high surface area, chemical inertness, non-toxicity, huge abundance, and low cost (Hu et al., 2013). On the other hand, the high bandgap energy (3.2 eV) and the low reaction kinetics would somewhat hinder the photocatalytic water-splitting performances.

To utilize solar energy effectively, many attempts have been made to modify the properties of TiO₂, such as doping with transition metal ions (Yang et al., 2012) or nonmetal anions (Meng et al., 2013), and sensitization with organic dyes (Jia et al., 2011). Among the nonmetal-doping TiO₂ photocatalysts, the simplest and most feasible TiO₂ modification approaches for achieving visible-light-driven photocatalysis seem to be N-doping, that is, doping nitrogen atoms into interstitial (or substitutional) sites in the crystal structure of TiO₂. To date, little research has been conducted on gaining in-depth information on the properties of the substitutional N-doped TiO₂, as well as its photocatalytic activity. Different dopants result in TiO₂ of different properties and consequently alter the photocatalytic activity of the materials. Currently, few works have focused on the synergistic effects of nitrogen dopant and calcination temperature on the characteristics and visible-light-induced photactivity of N-doped TiO₂ (Jia et al., 2011).

Accordingly, for efficient use of solar energy in photocatalytic reactions, it is important to extend the TiO₂ optical response into the visible light region (Peng et al., 2007). Therefore, the fabrication of nitrogen-doped TiO₂(N-TiO₂) of appreciable visible light absorptivity has been considered as a promising approach since the N-p derived states are generated immediately above the valence band (VB) causing band gap narrowing (Pei et al., 2013). It has been reported that interstitial nitrogen is supposed to have direct influences on the electronic states and light activities rather than substitutional ones (Deng et al., 2011).
Additionally, defect states originated from oxygen vacancies and reduced Ti species (Ti³⁺) in the band gap together with N-derived states are shown to contribute to the light absorption characteristics of N–TiO₂ in the visible light region (Zhang et al., 2011). Lately, a density functional theory has shown that N prefers to replace Ti rather than O to form NOx (Pei et al., 2013). Furthermore, oxygen vacancies near surface regions act as recombination centers and thus weaken the photocatalytic activities. The stability of N-doped TiO₂ is also an important issue of concern since it may be lost during treatments like calcination, solubilization, etc., resulting in decreased catalytic activity. Indeed, oxygen deficiencies and loss of nitrogen are not only affect the N-doped TiO₂ electronics but also influence the fast recombination of electron-hole pairs and thus affect seriously the photocatalytic efficacy. Hence, to prevent the recombination of charge carriers and to extend the light absorption into visible light region, a constructive conductive substrate is urgently required for enhancing the photocatalytic activity. The combination of TiO₂ with carbonaceous materials has attracted research attention since it enhances the efficiency of photocatalytic activity (Kuo, 2009). Particularly, graphene of magnificent electrical, mechanical, surface texturing and thermal properties has been incorporated with TiO₂ to form composites of high potential use in photocatalytic applications (Kongsong et al., 2018; Kovallevskiy et al., 2020). Introduction of TiO₂-based nanocomposites with graphene is simultaneously results in superior electron transfer owing to the excellent electrical conductivity of graphene (Chizari et al., 2012). At low loadings, graphene can work as an efficient electron conducting net-work (Ba et al., 2016). Accordingly, modification of TiO₂ nanomaterials with graphene or graphene oxide has shown great interests (Gomes et al., 2019), (Xie et al., 2013), (Yang et al., 2013), (Wang et al., 2009).

These outstanding features attracted graphene to be utilized as a promising support material to disperse and stabilize N-TiO₂ nanoparticles which in turn enhance the photocatalytic hydrogen production by water splitting containing sulphure. Some drawbacks can be effectively released by the hybridization of host photocatalysts (e.g., TiO₂) with highly-conjugated carbonaceous materials (e.g., activated carbon (AC), carbon nanotubes, graphitic carbon, graphene, graphene oxide, reduced graphene oxide, etc.) (Lin et al., 2022; Vu et al., 2021). Among them, graphene oxide nanostructures provide a strong interfacial interaction in between the photocatalyst species so that the rapid charge separation occurs and the electron-hole recombination rate decreases. This would eventually improve the hydrogen production efficiency during the photocatalytic wastewater splitting process. Graphene oxide has superior mechanical strength, excellent mobility of charge carriers, high thermal conductivity and large specific surface area. These outstanding features attracted graphene to be utilized as a promising support material to disperse and stabilize N-TiO₂ nanoparticles which in turn enhance the photocatalytic hydrogen production by water splitting containing sulphure.

Accordingly, loading TiO₂ nanocrystallities on major amounts of graphene or graphene oxide nanosheets will not improve the photocatalytic efficiency but indeed will increase the adsorption capability, which is not the issue and indeed not required. Increasing graphene nanosheet concentration is going to enlarge its aggregation around TiO₂ low contents affecting the latter good orientation towards light absorption and thus decreases the photoactivity. Due to the high oxygen functionality of graphene oxide, the interaction with N-TiO₂ is permitted for high wet-ability, disperse-ability and for obtaining both continuous and consistent nanophotocatalysts stable against light for longer time (Meiling et al., 2020; Lin-Wei et al., 2019).

Sulfide ions present in industrial wastes either as S₂- or hydrogen sulfide (H₂S) are toxic having an unpleasant odor. Petrochemical industry releases H₂S containing (15–20%) wastewater as a by-product, and their treatment process produces elemental sulfur. Also, sewage treatment plant releases the wastewater containing sulphide ion with concentration greater than 1200mg/L. At present a large amount of energy being spent for this treatment, whereas photocatalytic process can be effectively utilized to recover H₂ gas (Keishi et al., 2019; Minxue et al., 2019).

The nitrogen-doping of graphene will also change the affinity of graphene to hydrogen donor via hydrogen bond produced by nitrogen lone pair electrons, which is very useful for photocatalytic hydrogen production by water-splitting reaction. Owing to the effective impact of these factors on the electronic property and chemical reactivity of graphene, nitrogen-doped graphene (N-graphene) has been applied to synthesize the semiconductor nanocomposites as photocatalysts for hydrogen evolution, such as molybdenum disulfide/n-type nitrogen-doped reduced graphene oxide (Muhammad Aniq Shazni et al., 2019) and nitrogen-doped graphene/CdS (Chen-Chen et al., 2018).

In order comprehensively to explore the effect of nitrogen-doping on the photocatalytic efficiency of semiconductor nanocomposite of TiO₂ and graphene, N-TiO₂/GO- is synthesized herein as photocatalysts for hydrogen production through the in-situ nitrogen-doping of TiO₂ while the TiO₂/N-GO nanocomposite is prepared. The effects of the nitrogen content and the ratio of GO on the hydrogen production from sulphure present in the chemical industry were investigated. The effects of temperature, Ph and photooxidation times on the H₂ productions were researched and the reusability properties of the N-TiO₂/GO nanocomposite was analysed.

**Material and Methods**

**Synthesis of nitrogen-doped graphene oxide**

The mixture of lithium nitride (2.5 g) and tetrachloromethane (60 mL) was treated with ultrasonic dispersion for 20 min. Then the mixture was transferred into a 100-mL stainless steel autoclave and repeatedly deaerated by N₂. The reaction was carried out at 250°C for 10 h in nitrogen atmosphere. The product was washed sequentially with 10wt%HCl aqueous solution, distilled water, ethanol and freeze-dried. The resulting product was denoted as N-graphene. Samples using different
TiCl₂:urea ratios i.e. 35:1:2, 1:4 and 1:6 (w/w) were prepared. The N-TiO₂ was prepared by heat treating homogeneous 0.05 mole TiCl₄ and 0.2 mole urea (1:4 w/w of TiCl₂:urea) solution in absolute ethanol at 150°C to obtained an intermediate product (Ti-urea complex) which was further annealed at 300°C, 400°C and 500° 40 C for 3h. The product annealed at 300°C is named as T₂GO (with 2% loading) in absolute ethanol (without urea) at 150° 45°C to obtained the intermediate product which was further annealed at 300°C for 3h and denoted as T₃. The other products with dopants and graphene composites with 0.5%, 1% and 2% loading of GO were annealed at 300°C for 3h and denoted as T₄, T₅ and T₆, respectively.

These products were then subjected to XRD, UV-DRS, Raman, XPS, FTIR, FESEM, TEM and BET analysis for their characterization.

**Photodecomposition of H₂S**

The cylindrical quartz photochemical reactor was filled with 200 ml 0.25 M aqueous KOH and purged with argon for 1 h. Hydrogen sulphide (H₂S) containing chemical industry wastewater was bubbled through the solution for about 1h at the rate of 2.5 ml min⁻¹ at 299 K. Undoped TiO₂, N-TiO₂, TiO₂/GO and N-TiO₂ 60/GO (0.2 g) was introduced into the reactor and irradiated with a solar light. The escaped hydrogen sulfide was trapped in a NaOH solution. The amount of hydrogen gas was measured with Hatch Lange device. The evolved hydrogen was then analyzed for its purity using a gas chromatograph (Model Shimadzu GC-14B, MS-5 Å column. All the samples were tested for their catalytic activity under identical conditions for a continuous period of increasing minutes (30, 60 and 200 min).

**Characterization**

The crystalline phases and the crystallite size of the photocatalyst was identified using an X-ray powder diffraction (XRD) with Cu Kα irradiation. The optical properties of the powder samples were studied using an UV-visible-near infrared spectrometer. Room temperature micro Raman scattering (RS) was performed using a HR 800-Raman 80 Spectroscopy, France, with an excitation at 632.81 nm by a coherent He-Ne ion laser and a liquid nitrogen cooled CCD camera to collect and process the scattered data. The nature of chemical bonds formed in N-TiO₂ and GO were examined using X-ray photoelectron spectroscopy with a base pressure greater than 1.0 × 10⁻⁹ Pa and Mg Kα FTIR spectra’s were recorded with a spectrometer. The Brunauer-Emmett-Teller (BET) specific surface area (SBET) of the powders was analyzed by nitrogen adsorption apparatus.

**Results and Discussion**

**XRD analysis Results**

The peaks observed at 26.1°, 39.9°, 49.0°, 57.2°, 63.8°, 70.3° and 79.0° 30 are indexed as (102), (005), (202), (213), (206), (221) and (217) respectively (Figure 1). This indicates the formation of anatase crystalline structure. No peaks were observed for carbon species in the T3-T6 samples due to low amount of graphene. The observations indicates that the full width at half maximum is more for the anatase peaks of N-TiO₂ (T₂) which is attributed to the doping of nitrogen into the TiO₂ nanocomposite. In T3-T6 samples, the presence of increasing amount of graphene increase the degree of crystallization.

![Figure 1: XRD analysis in (a) undoped TiO₂ (T₁), (b) N-TiO₂ (T₂) (c) TiO₂ loading with 2% GO (T₃), N-TiO₂ loading with 0.5% GO (d) N-TiO₂ loading with 0.8% GO (T₄), (e) N-TiO₂ loading with 1% GO (T₅) and N-TiO₂ loading with 25% GO (f) (T₆)](attachment)
**UV-Vis diffuse reflectance spectra of TiO$_2$ solely (T1), N-TiO$_2$ (T2), iO$_2$/GO(T3), N-TiO$_2$-GO(T4-T6) nanocomposites**

The spectra shows the absorption edge at 389 nm (3.18 eV) for undoped TiO$_2$ (T1) as commonly observed for anatase TiO$_2$. The band gap energies of samples T$_2$-T$_6$ were determined to be 2.95 (424 nm), 2.58 (477 nm), 2.58 (486 nm), 2.55 (492 nm), 2.43 (517 nm) eV, respectively (Figure 2).

The extended visible light absorption edge was observed with increasing the graphene content in composite samples. It is obvious that N-TiO$_2$/GO shows much stronger absorption of visible light than TiO$_2$/GO nanocomposite. When N was doped into TiO$_2$ 60/GO nanocomposite, the absorption edge of T$_6$ sample is extended to 518 nm (2.43eV).

![Figure 2: UV-DRS spectra of (a) undoped TiO$_2$ samples (T$_1$) (b) N-TiO$_2$ (T$_2$) (c) TiO$_2$ containing 2% GO (T$_3$), N-TiO$_2$-containing 0.5% GO (d) (T$_4$), (e) N-TiO$_2$-containing 1% GO (T$_5$), N-TiO$_2$-containing 2% GO (f) (T$_6$).](image)

**Raman Spectrum**

The comparison of the Raman spectra of undoped TiO$_2$ (T1), N-TiO$_2$ (T2), TiO$_2$/GO (T3) and N-TiO$_2$/GO (T4-T6) samples showed that GO Raman spectrum shows two typical bands located at 1329 and 1595 cm$^{-1}$. These correspond to disordered sp$^2$ carbon and well ordered graphite carbon structures, respectively. Undoped TiO$_2$ (T1), exhibited several characteristic bands at 142, 394, 513, and 637 cm$^{-1}$. These can be corresponded with Eg (1), B1g(1), A1g+B1g(2) and Eg(2) modes of anatase, respectively. N-TiO$_2$ (T2), TiO$_2$/GO (T3) and N-TiO$_2$/GO (T4-T6) exhibited similarities with Raman bands mentioned for anatase. T3-T6 samples, exhibited Raman spectrum at D (1329 cm$^{-1}$) and G (1611 cm$^{-1}$) bands of graphene, indicating incorporation of GO in the all other nanocomposites.
Figure 3(A, B, C): Raman spectrum of samples (a) undoped TiO$_2$ (T1) (b) N-TiO$_2$ (T2) (c) TiO$_2$ with 2% GO (T3), N-TiO$_2$ with 0.5% GO (T4), (e) N-TiO$_2$ with 1.0% GO (T5), (f) N-TiO$_2$ with 2.0% GO (T6). (B) shows the magnified range from 1004-2004 cm$^{-1}$ (C) shows the magnified range from 2004-3004 cm$^{-1}$
For GO, Raman spectrum shows two typical bands located at 1328 and 1595 cm\(^{-1}\). These were correlated to sp\(^2\) carbon (D-band) and graphite carbon structures (G-band), respectively. Undoped TiO\(_2\) (T1), exhibited bands at 143, 395, 515, and 638 cm\(^{-1}\). These can be attributed to the Eg (1), B1g(1), A1g+B1g(2) and Eg(2) modes of anatase, respectively. N-TiO\(_2\) (T2), TiO\(_2\)/GO (T3) and N-TiO\(_2\)/GO (T4-T6) nanocomposites, exhibited Raman bands for anatase. The Raman spectrums in T3-T6 samples exhibited the D (1327 cm\(^{-1}\)) and G (1606 cm\(^{-1}\)) bands of GO, indicating the incorporation of graphene in the aforementioned nano composites.

Fig. 3(B) shows the Raman spectrum of all nanocomposites exclusively in the range of 1103-2003 cm\(^{-1}\). It was observed two dominated peaks centered at about 1327 cm\(^{-1}\) (D band) and 1607 cm\(^{-1}\) (G band) exhibiting the presence of graphene in the nanocomposites containing GO. The G band for samples (T3-T6) is broadened and red shifted to 1605 cm\(^{-1}\) after the reduction of GO (1593 cm\(^{-1}\)). This can be explained by Ti-O-C bond formation which exhibits a close interaction between TiO\(_2\) and GO and improving a strong integration across the interface between GO and anatase TiO\(_2\).

The band located at 283.6 eV can be assigned to the presence of the Ti-C bond. These bands exhibited the peak deconvolution of the Ti(2p) core level, as investigated in the Fig. 4 b shows the N(1s) core level spectrum where the peak at 399.7 eV can be attributed to the anionic N in O-Ti-N linkage while the peaks at 402.3 and 402.6 eV are ascribed to the molecularly chemisorbed γ-N\(_2\) and N-Ox surface species respectively. These peaks clearly indicate that nitrogen was substitutionally doped into TiO\(_2\) lattice. Fig. 4 c shows O(1s) narrow scan spectrum. The peaks around 531.9 eV and 533.1 eV are attributed to the Ti-O-Ti i.e. lattice oxygen and Ti-OH adsorbed on the sample surface, respectively.

In order to investigate the chemical changes occurred on the surface of the nanocomposite formation by during detection of the signals of N, Ti, O and C to elucidate the interaction between graphene, TiO\(_2\), and N-TiO\(_2\) nanocomposites. Fig. 4 shows the high resolution XPS spectra for C (1s), N (1s), O (1s) and Ti (2P) core levels of the N-TiO\(_2\)/GO nanocomposite. The XPS spectrum of C1S from GO is deconvoluted into three peaks which are ascribed to the following functional groups: Sp2 bonded carbon (C-C, 285.6 eV), epoxyl/hydroxyls (C-O, 288 eV), carbonyls (C=O, 286.9 eV) (data not shown). The first peak indicates the presence of 2D carbon structure, the latter two peaks indicate the presence of high percentage of oxygen-containing functional groups. The XPS spectrum of C(1s) from N-TiO\(_2\)/GO shows that the peak intensity for oxygen containing functional groups substantially lowered as compared to the intensity for oxygen containing functional groups in the spectrum of GO (Fig. 4a). The band located at 283.6 eV can be assigned to the presence of the Ti-C bond. These bands exhibited the peak deconvolution of the Ti(2p) core level, as investigated in the Fig. 4 b shows the N(1s) core level spectrum where the peak at 399.7 eV can be attributed to the anionic N in O-Ti-N linkage while the peaks at 402.3 and 402.6 eV are ascribed to the molecularly chemisorbed γ-N\(_2\) and N-Ox surface species respectively. These peaks clearly indicate that nitrogen was substitutionally doped into TiO\(_2\) lattice. Fig. 4 c shows O(1s) narrow scan spectrum. The peaks around 531.9 eV and 533.1 eV are attributed to the Ti-O-Ti i.e. lattice oxygen and Ti-OH adsorbed on the sample surface, respectively.

Since GO are excellent electron 60 acceptors, the Ti-C and Ti-O-C bonds can act as effective channels in electron transferring from the photoexcited N-TiO\(_2\).
FTIR spectra
The GO displayed several characteristic absorption bands of oxygen containing groups (Fig. 5 A). The IR absorption at 1727 cm⁻¹ could be attributed to the C=O stretching vibration. The peak at around 964 cm⁻¹, 1057 cm⁻¹, 1252 cm⁻¹ corresponds to the epoxy stretching, alkoxy C-O stretching and C-O-C stretching peaks, respectively. The broad band at 1562 cm⁻¹ can be assigned to in-plane vibrations of aromatic C=C Sp² hybridized carbons. As against the evidence of these oxygen-containing groups of GO, the absence small intensity of bands of oxygen containing functional groups (C-O, C-O-C) in samples (T3-T6) was noteworthy (Fig. 5B). T1 and T2 samples show presence of sharp Ti-O-Ti bands in their IR studies at 652 cm⁻¹. Oxygen containing groups mentioned above must have reacted with the species which are in close contact with GO, namely Ti. However, the broadening of Ti-O-Ti peak suggests the presence of a peak due to Ti-O-C bond. Thus, Ti-O-Ti bonding is well understood.

H₂ production from H₂S
Table 1 shows the hydrogen production from the photodecomposition of H₂S using undoped TiO₂ (T1), N-TiO₂ (T2), TiO₂/GO (T3) and N-TiO₂ /GO (T4-T6). Control researches indicated no significant hydrogen production was detected in the absence of irradiation or photocatalyst samples. This showed that hydrogen is produced only through photocatalytic reaction. Undoped TiO₂ shows low hydrogen production compared to the other nanocomposites. N-TiO₂ containing 2% GO exhibited the highest hydrogen production of 8976 mol/min during 60 min photooxidation. N-TiO₂ containing no GO exhibited a hydrogen production rate of around 3470 mol/min. This can be attributed to N doping in TiO₂ enhances hydrogen evolution rate. By incorporating of GO at a ratio of 2% to N-TiO₂ elevated the hydrogen production 3 times compared to undoped TiO₂. As a result hydrogen production increased by increase of GO percentage. Hydrogen evolution increases with increasing graphene content (see Table 1). However, further increasing the amount of graphene affects the hydrogen production which is unfavorable beyond 2%. The active sites of N-TiO₂ may not covered fully by 2% GO. Indeed, This GO ratio was not lead to shielding of the active sites on the nanocatalyst surface and also did not decrease the intensity of light through the depth of the reaction solution.

Figure 4: XPS patterns of N-TiO₂ with 2% GO loading (T6) (a) C(1s), (b) N(1s), (c) O(1s), (d) Ti(2p).

Figure 5(A, B): FTIR spectra of samples (A) GO, (B) (a) undoped TiO₂ (T1) (b) N-TiO₂ (T2) (c) TiO₂ with 2% GO (T3), N-TiO₂ with 0.5% GO (d) (T4), (e) N-TiO₂ with 1% GO (T5), N-TiO₂ with 2% GO (f) (T6).
Effects of Ni/TiO2 / GO Ratios and pH variations on H2 production rate

The maximum H2 yields was detected at high GO ratios as 12300 mol/min at pH=7 (Table 2).The GO in the nanocomposite is as an electron acceptor and transporter. GO has been reported to be competitive candidate as an acceptor material due to its π-conjugation structure and has excellent mobility of charge carriers and large specific surface area. Therefore, rapid transport of charge carriers could be achieved and an effective charge separation consequently accomplished. Overall, both the electron accepting and transporting properties of graphene in the nanocomposite could contribute to the enhancement of photocatalytic activity. Additionally, as per the PL study, the lower intensity peaks observed in graphene doped samples indicating that the electron-hole recombination on the surface of catalysts is largely inhibited to generate more free photoelectrons and holes. Hence, the enhanced photocatalytic activity of N/TiO2 / GO nanocomposite with a ratio of 1/1/3 is mainly attributed to more effective charge transportation and separation arisen from the strong chemical bonding of N-TiO2 and GO.

Sample properties | S -BET (micronmeter) | H2 production mol/ min |
--- | --- | --- |
Undoped TiO2 | 98 | 2340 |
N-TiO2 with no GO | 103 | 3470 |
TiO2 with 0.1% GO | 134 | 4500 |
N-TiO2 with 0.5% GO | 208 | 6987 |
N-TiO2 with 1% GO | 221 | 7897 |
N-TiO2 with 2% GO | 243 | 8976 |

Table 1: BET and H2 Productions in different types of nanocomposite compositions

Effects of Ni/TiO2/GO Ratios and pH variations on H2 production rate

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Sample properties | S -BET (micronmeter) | H2 production mol/ min |
--- | --- | --- |
N/TiO2/GO =3/1/1 | 223 | 3200 3200 4000 |
N/TiO2/GO= 1/3/1 | 229 | 5437 9752 6900 |
N/TiO2 / GO =1/1/3 | 259 | 7654 12300 8760 |

Table 2: Variations of H2 production rates versus Ni/TiO2 / GO ratios and pH

The H2 production from H2S under visible-light irradiation with N/TiO2 / GO nanocomposite are as follows:

\[
\begin{align*}
\text{H}_2\text{S} + \text{OH}^- &\rightarrow \text{HS}^- + \text{H}_2\text{O} \\
\text{N/TiO}_2 / \text{GO nanocomposite} &\rightarrow \text{N/TiO}_2 (\text{h}^+) + \text{GO} (\text{e}^-) \\
\text{Oxidation 2HS}^- + \text{N-TiO}_2 (2\text{h}^+) &\rightarrow 28 + 2\text{H}^- \\
\text{Reduction 2H}^+ + \text{GO} (2\text{e}^-) &\rightarrow \text{H}_2
\end{align*}
\]

Transport of electrons from TiO2 to GO is energetically a favorable process. Thus, efficiently separation of photo-induced charge carriers leads to lowering of charge recombination and effectively enhance the photocatalytic performance. These electrons are accessible to the adsorbed H+ ions to form H2. Therefore, the synergistic effect of H2 production on catalyst surface is because of extended visible light absorption due to ‘N’ doping, optimal GO ratio and efficient charge separation by photocatalytic H2S splitting to H2 with suitable TiO2/ N / GO nanocatalyst ratios.

Effects of increasing temperatures and photooxidation times on H2 production rate

Table 3a and 3b shows the H2 productions versus increasing temperatures and photooxidation times at different nanocomposite components. The effectiveness of N/TiO2 / GO nanocatalyst was evaluated by investigating the effect of temperature at different contact times on H2 production. H2 production increases with temperature because reforming and decomposition reactions; both are very endothermic reactions; as a result, a small increase in temperature results in a significant increase in H2 production. The hydrogen concentration increases from 7698 mol/min up to 12987 mol/min as the temperature was increased from 18°C to 30°C. Increasing of temperature to 41°C did not increase significantly the H2 production significantly.

The product yield increases with photooxidation time. At low photooxidation time such as 30 min the H2 productions was low as the photooxidation time was increased to 60 min the maximum H2 productions was detected. At long photooxidation time the H2 productions lowered.

<table>
<thead>
<tr>
<th>Sample properties</th>
<th>H2 production mol/min</th>
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<tbody>
<tr>
<td>Temperature (°C)</td>
<td>18 31 45</td>
</tr>
<tr>
<td>N/TiO2/GO =3/1/1</td>
<td>3200 4856 4100</td>
</tr>
<tr>
<td>N/TiO2 / GO= 1/3/1</td>
<td>5499 9752 6986</td>
</tr>
<tr>
<td>N/TiO2 / GO =1/1/3</td>
<td>7698 12987 11760</td>
</tr>
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Table 3a: Effect of temperature on H2 production

<table>
<thead>
<tr>
<th>Sample properties</th>
<th>H2 production mol/min</th>
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<tbody>
<tr>
<td>Photooxidation time (min)</td>
<td>30 60 200</td>
</tr>
<tr>
<td>N/TiO2/GO =3/1/1</td>
<td>3180 4856 4200</td>
</tr>
<tr>
<td>N/TiO2 / GO= 1/3/1</td>
<td>5487 9745 6970</td>
</tr>
<tr>
<td>N/TiO2 / GO =1/1/3</td>
<td>7675 12956 11855</td>
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Table 3b: Effects of increasing photooxidation time on H2 production rate

<table>
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<tr>
<th>Sample properties</th>
<th>H2 production mol/ min</th>
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| N/TiO2 / GO nanocomposite describes its economic behavior and shows the reprocessing capability up to n number of cycles. In the first cycles the H2 production rates was not lowered after 12 000 minutes and 400 cycles while the H2 production was recorded as 11987 mol/min after 2000 min and 660 cycles utilization of the same nanocomposite (Table 4).

Reuse of N/TiO2 / GO nanocomposite

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Table 4: Recovery of N/TiO₂ / GO nanocomposite

<table>
<thead>
<tr>
<th>Photooxidation time (min)</th>
<th>H₂ production mol/ min</th>
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<tr>
<td>30</td>
<td>12900</td>
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<td>60</td>
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<td>11989</td>
</tr>
<tr>
<td>20000</td>
<td>11989</td>
</tr>
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**Conclusions**

N/GO/TiO₂ nanocomposite was produced under laboratory conditions to produce photocatalytic hydrogen production from H₂S. The same nanocomposite was used 660 times for 2000 min with a H₂ production of 11987 mol/min after 2000 min and 660 by using 1.2 mg N/TiO₂ / GO nanocomposite with a ratio of 1/1/3. The optimal conditions for maximal H₂ production of 12956 mol/MIN were 30 min photooxidation time at pH = 7.0 and at a temperature of 31°C.

**References**


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