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Fabricating Carbon Fibers (CFs)/TiO_2 Composite for Photocatalytic Green Hydrogen Production

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The current energy crisis and environmental pollution problems can be efficiently resolved by photocatalytic hydrogen production using the water-splitting process. The key to this method is the development of highly efficient and low-cost semiconductor photocatalysts. In this work, CFs (carbon fibers) were synthesized using solid waste carbon fiber-reinforced polymer (CFRP) and were coupled with TiO_2 to construct heterojunction to increase photocatalytic hydrogen evolution efficiency. Using optimized 3 % CFs/TiO_2, H_2 yield rate of 85.4 μmol g^{-1} h^{-1} was obtained, which was 2.87-fold higher than using pure TiO_2. Increased visible light absorption and effective photoinduced charge carrier separation were the causes of this increase in hydrogen generation. This study provides an alternative approach to recycling solid waste materials into valuable products that may improve semiconductor performance in solar energy-related applications.

1. Introduction

Photocatalytic hydrogen (H_2) production through water splitting has emerged as a promising and desirable technology to solve the problems of energy and environmental issues (Baamran et al., 2021). Solar energy is particularly appealing for H_2 production as a sustainable fuel to mitigate carbon dioxide (CO_2) emissions. Although photocatalysis is promising, it is crucial to produce effective, affordable, and stable semiconductor materials with higher photocatalytic efficiency and acceptable stability.

In previous years, several types of photocatalysts such as graphitic carbon nitride (Tasleem et al., 2023), titanium dioxide (TiO_2), zinc oxide (ZnO), cadmium sulfide (CdS) (Xue et al., 2023), and tungsten oxide (WO_3) (Mo et al., 2023) have been studied for hydrogen production. Among all, TiO_2 is a viable material for producing H_2 because it has several benefits, such as being inexpensive, chemically stable, non-toxic, and higher oxidation potential. Its photocatalytic activity, however, is lower due to the high electron-hole recombination rate (Tahir 2018). The photocatalytic efficiency of TiO_2 can be enhanced by using several ways, including sensitizing with metals as cocatalysts and fabricating semiconductor composites (Beenish et al., 2018). For example, Ni_2P and MAX were attached to TiO_2 to enhance photocatalytic efficiency due to efficient charge carrier separation (Tasleem et al., 2023). Coupling g-C_3N_4 and CdS with TiO_2 to construct a ternary composite was beneficial to enhance TiO_2 photoactivity, resulting in significantly improved H_2 production. Many metals and semiconductors such as Au/WO_3 (Tahir et al., 2020), and Ag/g-C_3N_4 (Fajrina et al., 2019) were used with TiO_2 to enhance the H_2 production rate. Instead of using expensive metals and semiconductors, TiO_2 performance can be improved using environmentally friendly and low-cost materials.

Carbon fiber-reinforced plastic (CFRPs) is a promising material that uses carbon fibers as the reinforcement and epoxy resin as the matrix. It is one of the most significant carbon fiber-based products in industrial applications. Due to its low density, high strength, and desirable comprehensive features, CFRPs have become popular in various applications (Pei et al., 2022). Overuse of these materials has raised awareness of the need to recycle CFRP trash on the environmental and economic fronts. Pure carbon fibers (CFs) made from solid CFRPs waste can be highly conductive materials in semiconducting applications (Akbar et al., 2020). This is so that electrons can be trapped and transported within the semiconductor via CFs, a metal-free source. Since they are inexpensive and have excellent electrical conductivity, they can also serve as cocatalysts. Previously, bamboo charcoal loaded g-C_3N_4 to increase H_2 efficiency were reported (Wang et al., 2022). Utilizing CFRPs-

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derived CFs with TiO_2 to construct CFs/TiO_2 composite would be promising to enhance the water splitting process for hydrogen production with higher photostability.

In this work, recycling CFRPs to produce highly efficient CFs as cocatalysts with TiO_2 to construct CFs/TiO_2 composite for photocatalytic H_2 production has been investigated. The use of pyrolysis of CFRPs obtained the CFs. The CFs/TiO_2 composite was synthesized using a self-assembly approach. The photocatalytic H_2 production experiments were conducted using a slurry photoreactor with a methanol sacrificial reagent. The effect of CFs loading was further investigated, and their performance was compared. The schematic mechanism was proposed based on the characterization and experimental results.

2. Experimental

2.1 Catalyst Synthesis

The CFs were obtained by using a pyrolysis approach with the use of CFRPs as the raw material. Typically, CFRP sheets, after cutting into smaller rectangular shapes, were heated in a tube furnace for 2 h at 350 °C to eliminate polymeric material. After being removed from the furnace, the finished product was ground into a fine powder. The CFs/TiO_2 composite was synthesized using a physical mixing approach. For this purpose, the anatase phase of TiO_2 (Titanium dioxide anatase powder, Sigma-Aldrich, 99.8%) was used to produce CFs/TiO_2 composite. In a typical procedure, initially, TiO_2 was dispersed in methanol for 30 min, followed by adding CFs dispersed in methanol under continuous stirring. The mixture was stirred for 2 h at room temperature and oven dried at 100 °C for 24 h and was named as CFs/TiO_2 composite. Different CFs amounts were added to TiO_2 using the same process to get 2, 3 and 4 wt. % CFs/TiO_2.

2.2 Materials Characterization

The products were analyzed using several techniques. Using X-ray diffraction (XRD), samples were asses for their purity with Bruker Advance D8 diffractometer. Using a HORIBA Scientific Spectrophotometer, a Raman and photoluminescence (PL) investigations were performed (laser 532 nm). Scanning electron microscopy (SEM) was used to determine morphology (Hitachi SU8020). The optical response of the materials was examined using a diffuse reflectance spectrometer (DRS) in the UV-visible range (UV-3600 Plus Spectrometer).

2.3 Photocatalytic Activity Test

The performance of photocatalysts was measured using a slurry-type photoreactor system with total volume of 100 mL. The light source was a 35 W Xenon lamp with an intensity 20 mW/cm^2, and it was used without UV-cut filters. The photocatalyst was uniformly mixed with the solution through magnetic stirring. The products were analyzed using online gas chromatography (INFICON µGC). All the experiments were conducted on continuous operation, and products were analyzed continuously over the irradiation time. With 5 vol. % methanol and 100 mg of photocatalyst loaded, the performance of the pure and composite photocatalysts was evaluated.

3. Results and Discussion

3.1 Materials Analysis

The morphology of the pure CFs, TiO_2 and CFs-loaded TiO_2 composite was examined using scanning electron microscopy (SEM) and the results are presented in Figure 1. Figure 1 (a) shows large diameter CF fibres, which were produced after pyrolysis of CFRP. It can confirm that CFs can be successfully produced using the pyrolysis approach. Uniform-size TiO_2 particles can be seen in Figure 1 (b). The TiO_2 was obtained from Sigma-Aldrich, and displays TiO_2 particles of uniform size. Figure 1 (c-d) shows the morphology of the CF/TiO_2 composite obtained after physical mixing. It could be observed that TiO_2 particles are attached to CFs to construct heterojunction. More importantly, large-size carbon fibers were broken into smaller size, possibly due to grinding process. Previously, uniform size CFs were reported, which were produced using carbon fiber cloth (Guo et al. 2022).

Figure 2 (a) shows XRD patterns of TiO_2 and CFs/TiO_2 composites. The XRD patterns of TiO_2 show several peaks indexed to (101), (004), (200), (105), (211) and (204) facets, which confirmed TiO_2 anatase phase (Tahir et al. 2023). When CFs were loaded with TiO_2, similar XRD patterns were observed, which confirms the successful fabrication of CFs/TiO_2 composite. The XRD pattern for CFs was not identified due to its amorphous structure and lower amount of loading. These findings demonstrate that the CFs/TiO_2 composite was successfully made without any impurities. Figure 2 (b) displays the Raman spectra of the TiO_2 and CFs/TiO_2 composite samples. Raman peaks for the pure anatase phase of TiO_2 were observed at 141.9, 196.5, 397.8, 516.9, and 640.7 cm^{-1}. When CF was introduced to TiO_2, there was a shift in peak positions. The major peak formed at 143.7 cm^{-1}, indicating a successful production of the CFs due to good interaction between the two materials. This suggests that the CF-based TiO_2 composites were successfully made without any changes to the phase structure or the addition of any other impurities.

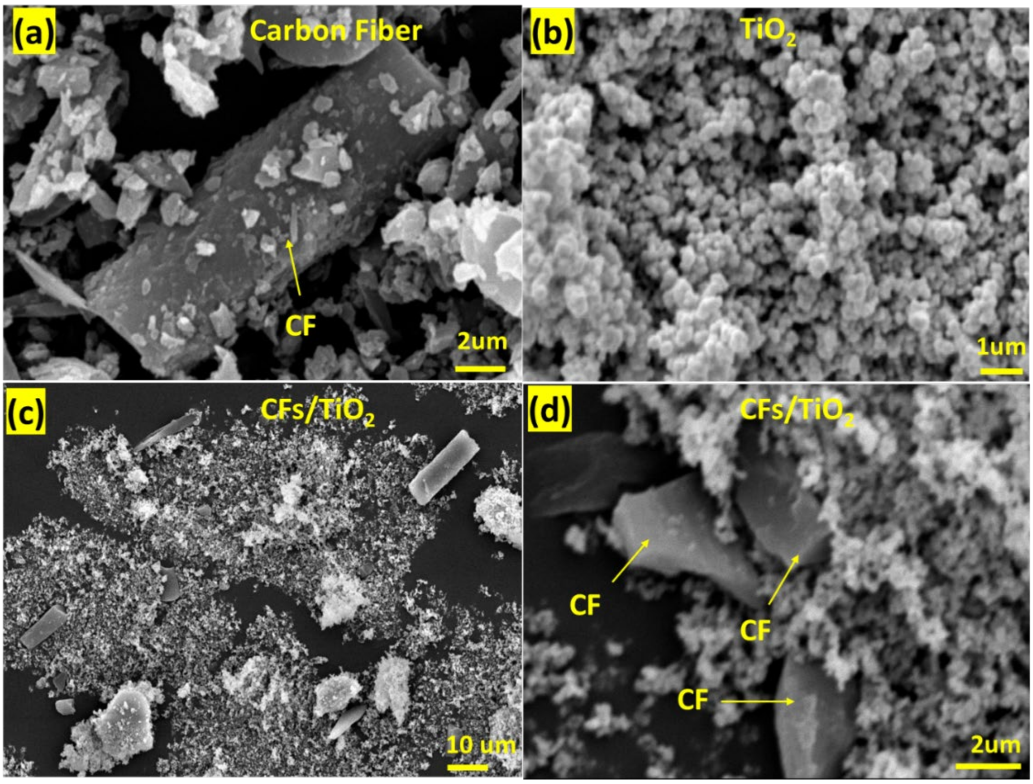

Figure 1: SEM analysis of (a) CFs, (b) TiO_2, and (c-d) CFs/TiO_2 composite samples.

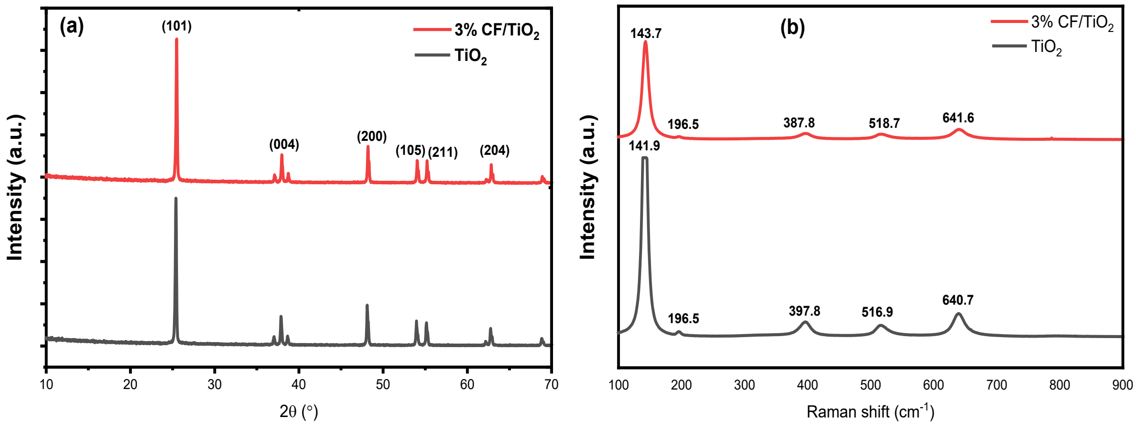

Figure 2: (a) XRD patterns of TiO_2 and CFs/TiO_2, (b) RAMAN analysis of TiO_2 and CFs/TiO_2.

The UV-vis diffuse reflectance absorbance spectra of the TiO_2 and CFs/TiO_2 composites are shown in Figure 3 (a). Pure TiO_2 shows light absorbance in the UV-visible light region. When CFs were loaded with TiO_2 to construct a CFs/TiO_2 composite, light absorption efficiency was increased compared to TiO_2 nanoparticles. This reveals that CFs as a cocatalyst are promising to increase visible light absorption of the TiO_2, promising to enhance photocatalytic efficiency. When CFs were loaded to $g\text{-}C_3N_4/TiO_2$ composite, visible light absorbance was increased (Guo et al., 2022).

The charge recombination of the pure and the composite of TiO_2 and CFs/TiO_2 was further investigated using Photoluminescence (PL) analysis, and the results are presented in Figure 3 (b). In general, PL tests assess how well electron-hole pair separation works. In general, high photoluminescence intensity is correlated with low photocatalytic activity and high electron-hole pair recombination efficiency (Tahir et al., 2021). Pure TiO_2 has higher PL intensity, which shows higher charge recombination using pure materials. When CFs were loaded with TiO_2, a much lower PL intensity was observed. This reveals that CFs are promising as a cocatalyst to trap and transport photoinduced charge carriers within the composite surface.

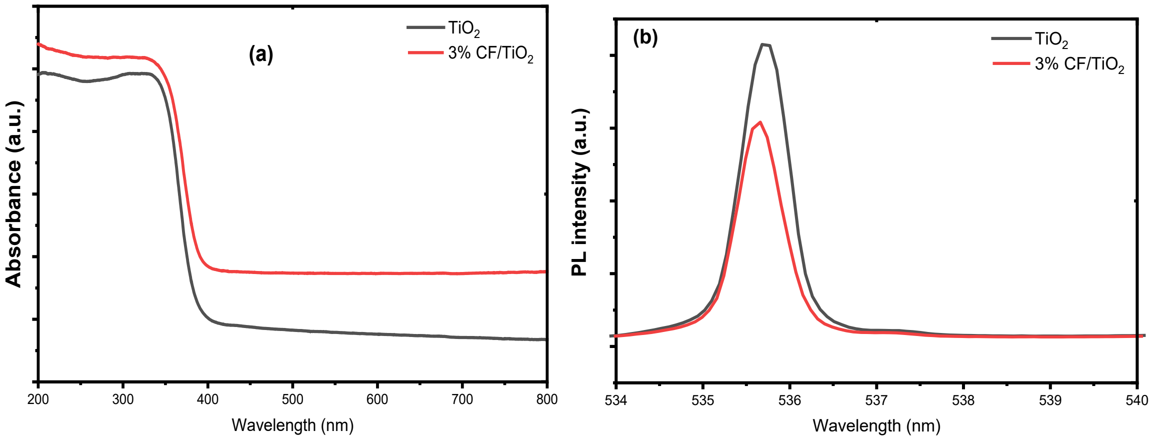

Figure 3: (a) UV-visible DRS of TiO_2 and CFs/TiO_2 and (b) PL analysis of TiO_2 and CFs/TiO_2 samples.

3.2 Photocatalytic hydrogen production

Figure 4 (a) shows the performance of TiO_2 and CFs/TiO_2 with various CFs loadings (2 to 5 wt. %) for photocatalytic H_2 production at various times. Using pure TiO_2, continuous production of hydrogen was observed over the entire irradiation time. The H_2 yield was lower compared to all other samples in which CFs were loaded. When 2 % CFs were loaded, much higher and continuous production of H_2 was observed. The highest H_2 production was achieved when optimized 3 wt. % CFs were loaded with TiO_2. After 90 minutes of irradiation, the production was somewhat reduced. The decrease in photocatalytic activity over time compared to TiO_2 would possibly be due to the separation of CFs from TiO_2 under continuous stirring, which were physically attached.

Figure 4 (b) shows the performance analysis of pure TiO_2 with various CFs-loaded TiO_2 samples. Using TiO_2, the H_2 yield rate of 29.7 μmol g^{-1} h^{-1}, was significantly increased with CFs-loading. The optimized CFs loading of 3 wt. %, yielded H_2 production rate of 85.4 μmol g^{-1} $h^{-1,}$ which is 1.11, 2.20, and 2.88-fold more than using 4 % CFs/TiO_2, 2 % CFs/TiO_2 and pure TiO_2 samples. The productivity of hydrogen was significantly enhanced by the conductive characteristics of CFs, which was beneficial to increase the separation of electrons from the TiO_2 surface (Li et al., 2022). When CFs loading was increased above 3 wt. %, the production of H_2 was decreased. This could be possibly due to more coverage of TiO_2 surface by CFs, and it would also be due to charge carrier recombination centers, resulting in higher photocatalytic efficiency for H_2 production.

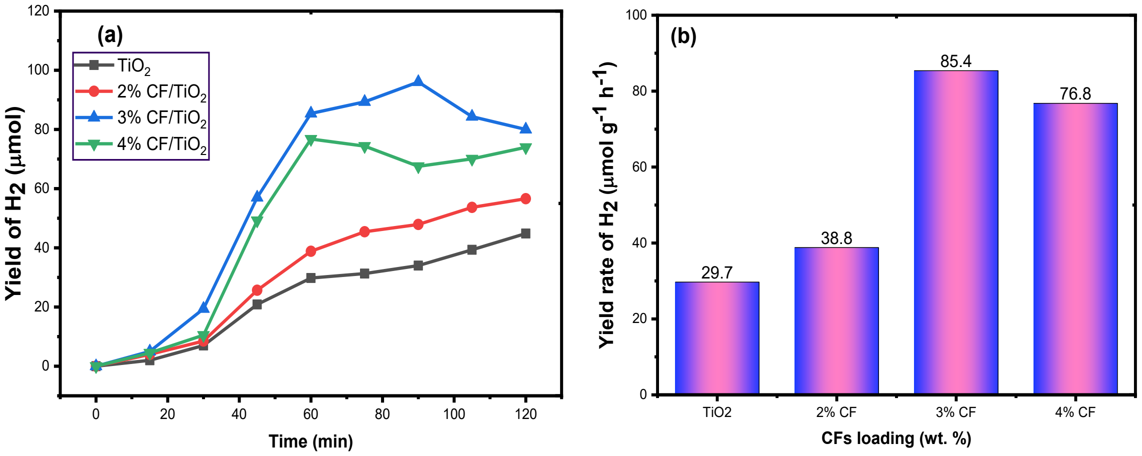

Figure 4: (a) Effect of CFs loading on the performance of TiO_2 at various irradiation times for photocatalytic H_2 production, (b) Performance comparison of TiO_2 and CFs/TiO_2 for H_2 production.

In the literature, several articles report using carbon fibers from various sources as support and cocatalyst to enhance semiconductor photocatalytic activity. For example, when carbon fibers, derived from spent cigarette filters, were used as a support with $ZnIn_2S_4$ and g-C_3N_4 to construct heterojunction, an enhanced hydrogen evolution rate was obtained. In this case, CFs provide a driving force to extract the photoinduced electrons from the heterojunction to participate in the reduction reaction (Yang et al., 2023). In another work CFs were loaded with TiO_2 to construct CFs/TiO_2, which was found promising in photocatalytic degradation applications (Cheng et al., 2021). Similarly, when NiO/TiO_2 was supported over carbon nanosheets, a much higher H_2 production efficiency was achieved (Zhao et al., 2020). All these findings confirm that carbon-based materials can be used as a cocatalyst to promote semiconductor photocatalytic efficiency.

3.3 Reaction Mechanism

In photocatalytic applications, the process of charge generation and their effective separation is helpful to get more information about the reaction mechanism. According to results obtained over CFs/TiO_2, it is evident that CFs works as a catalyst to trap and transport photoinduced charge carrier. The schematic mechanism of photoinduced charge production and separation has been demonstrated in Figure 5. When exposed to light, the TiO_2 surface produces electrons (e^-) and holes (h^+), which can then participate in various oxidation and reduction reactions. CFs work as a cocatalyst, and electrons are trapped and transported by CFs to participate in reduction reaction to produce H_2. Since TiO_2 and CF work well together as cocatalysts, CF's conductive qualities would effectively trap electrons from TiO_2 during the response. At the same time, the electrons captured by CF would be further employed for H^+ reduction to make H_2 with the involvement of two electrons and two holes. The holes maintained at VB of TiO_2 are additionally utilized for protons (H^+) production through water oxidation. The enhanced visible light absorption and reduced charges recombination rate of TiO_2/CF have recently been shown to have higher photocatalytic H_2 evolution rates (Tahir et al., 2023). The CF/TiO_2 was found to be promising due to its unique properties, such as its wide surface area, low bandgap energy, and charge separation efficiency to significantly improve photocatalytic H_2 evolution.

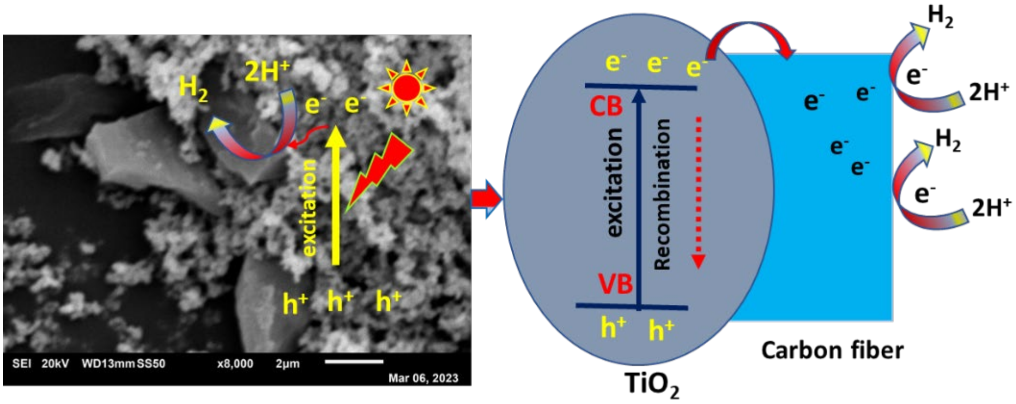

Figure 5: Schematic presentation of the proposed CFs/TiO_2 composite mechanism for photocatalytic H_2 evolution under UV-visible light irradiation.

4. Conclusions

In conclusion, CFs were successfully produced from CFRP through the pyrolysis process. The composite of CFs/TiO_2 was synthesized using a physical mixing method and was tested for photocatalytic H_2 production. The CFs showed improved visible light absorption with greater charge separation efficiency. Compared to pristine TiO_2, a much higher H_2 yield was achieved using CFs/TiO_2 due to the increasing lifetime of electrons by CFs. With 3 % CFs/TiO_2, the maximum H_2 generation of 85.4 $\mu mol\ g^{-1}\ h^{-1}$ was achieved, 2.88 times higher than using only TiO_2. This work demonstrates that waste materials like CFRPs and others can be recycled to more useful materials and used as cocatalysts for photocatalytic applications. This work has limitations of TiO_2 photoactivity under UV light and lower interface interaction of TiO_2 with CFs, which can be resolved by constructing heterojunction with semiconductor and using the sol-gel method of catalyst preparation. The findings of this work would be beneficial to further explore CFs as cocatalysts for other energy and cleaner process applications.

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