



Novel Multiphase CO₂ Photocatalysis System Using N-TiO₂/CNCs and CO₂ Nanobubble

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Abstract. In this study, a novel CO₂ photocatalysis system was developed by modifying TiO₂ as a photocatalyst and introducing CO₂ nanobubble to the system. TiO₂ photocatalyst is modified by adding CNCs as support to increase the surface area and adding nitrogen doping to reduce the band gap and minimize electron-hole recombination. CO₂ nanobubbles are introduced to increase the surface area between the CO₂ gas and liquid phases to reduce mass transfer limitations. Thus, the amount of CO₂ in the liquid phase increases. Nanobubbles have been successfully generated by the hydrodynamic cavitation method, which produces bubbles with two size clusters, namely 200–400 nm, which belong to nanobubbles, and 2–10 μm, which belong to microbubbles. The TiO₂ has an anatase phase and crystallite size of 20.90 nm for TiO₂/CNCs and 19.20 nm for N-TiO₂/CNCs. The activity test without nitrogen doping produced a methanol product of 0.77 mmol/g catalyst, which shows that this multiphase CO₂ photocatalytic system is feasible for CO₂ photocatalytic reactions. The addition of nitrogen doping succeeded in reducing the band gap from 3.20 eV to 3.10 eV and increasing the methanol yield. The photocatalysis activity test with N-doped TiO₂/CNCs resulted in a higher methanol yield, which is 1.13 mmol/g catalyst under UV-C irradiation for 6 hours.

Keywords: CO₂ photocatalysis; Multiphase reaction; Nanobubble; Nitrogen doping; TiO₂

1. Introduction

CO₂ photocatalysis is an appealing solution to reduce CO₂ on the earth's surface because this method not only can reduce CO₂ but also can provide solar fuels (CH₄, CH₃OH, HCHO, HCOOH) as an alternative to fossil energy (Shao *et al.*, 2022). TiO₂ is the most used semiconductor for CO₂ photocatalysis due to its non-toxic characteristics, high energy potential, and low cost. However, TiO₂ has a low photoconversion rate due to its high band gap, which results in a high energy requirement for electron excitation, electron-hole recombination, a low ability to absorb sunlight, and a low ability to adsorb CO₂ (Low, Cheng, and Yu, 2017). Thus, TiO₂ needs to be modified further to improve its performance

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so that the photocatalytic reaction becomes more efficient.

TiO₂ can be modified in various ways, such as the addition of co-catalysts and doping. The effects of co-catalysts and doping can vary based on the type of atom used. Some examples of co-catalysts are Ag, Co, and Cu. The addition of a plasmonic Ag metal core can increase the photon flux on TiO₂, which can increase the CO₂ photocatalysis conversion (Hong *et al.*, 2019). A co-based co-catalyst can increase CO₂ adsorption capacity and provide more CO₂ in the reaction (Zhang *et al.*, 2020). Cu co-catalyst is more beneficial for CO₂ adsorption and a good co-catalyst for improving catalytic selectivity to CH₃OH (Xi *et al.*, 2022). Doping is another type of TiO₂ modification that can use metal or non-metal atoms as dopants. The addition of dopant didn't lead to a structural defect that occurs in co-catalyst modification, which is an advantage of doping modification if compared with co-catalyst. An example of TiO₂ modification with doping is using N and Mo. N-doping can reduce the band gap and minimize electron-hole recombination. In addition to lowering the band gap, nitrogen doping can minimize electron-hole recombination by filling the oxygen defect in TiO₂, which is the key recombination site (Kumar, Das, and Deepa, 2020). Mo-doping can increase the selectivity toward CH₄ products and increase electron-hole separation and proton supply (Feng *et al.*, 2020). A smaller band gap allows electrons to be excited by lower energy light so that photocatalysts can be used in visible light irradiation. For example, as Kumar, Das, and Deepa (2020) reported, nitrogen doping can lower the band gap of TiO₂/CdS from 3.17 eV to 2.91 eV.

Besides using co-catalyst and doping, TiO₂ can also be modified by creating a mesoporous structure, which can increase the active site of the photocatalyst. For example, Yudha *et al.* (2020) use dammar-gum as a soft template for mesoporous TiO₂ synthesis. Another interesting material that can be used for mesoporous TiO₂ templates is cellulose nanocrystals (CNCs) (Chen *et al.*, 2016). CNCs are cellulose-based nanomaterial with high crystallinity, between 54–88% (Moon *et al.*, 2011). CNCs are renewable materials that can be made from various sources containing cellulose, such as wood (Leung *et al.*, 2011), flax (Leung *et al.*, 2011), empty palm oil bunch (Harahap *et al.*, 2023; Marpongahtun *et al.*, 2023; Budhi *et al.*, 2018; Wibowo *et al.*, 2018), and other lignocellulosic materials (Restiawaty *et al.*, 2022). Even CNCs can be produced from waste materials containing cellulose, such as paper and denim waste (Culsum *et al.*, 2021). CNCs have several superior properties, such as high mechanical properties, high surface area, high biocompatibility, and low toxicity (Brinchi *et al.*, 2013). With renewable sources of raw materials and superior properties, CNCs can be a long-term alternative green material for various purposes. CNCs can be used as a material to support various catalysts, one of which is TiO₂. Maimaiti *et al.* (2019) conducted a study related to TiO₂ photocatalysts dispersed on the surface of CNCs with the addition of EDA treatment. The photocatalyst produced 4.5 times more products than pure TiO₂ (P25) photocatalyst. The small size of CNCs causes a large surface area that increases the surface area of the TiO₂ photocatalyst active center. With many active centers, the number of products produced is also greater.

Besides photocatalyst modification, CO₂ photocatalytic conversion can also be increased by improving the photocatalytic process. In multiphase system, the mass transfer limitation become a hindrance for CO₂ conversion. To overcome the issue of CO₂ mass transfer limitation in a multiphase system, reducing the bubble size to the smallest possible can increase the contact surface area between the gas and liquid phases. In addition, the smaller bubble size can produce a larger mass transfer coefficient ($k_L a$) so that the mass transfer of CO₂ from the gas phase to the liquid phase becomes faster. Nanobubbles are defined as gas bubbles that have a diameter smaller than 1000 nm. The use of nanobubbles over regular bubbles in a process has various advantages, including high mass transfer

efficiency, high bubble stability, and low rising velocity (Ulatowski *et al.*, 2019). The utilization of nanobubble in chemical reactions remains relatively limited. Nevertheless, its application exhibits considerable potential. For example, Mase *et al.* (2013) reported a significant enhancement in the conversion rate from 2% to 99% in the hydrogenation of alkenes through the usage of nanobubble.

In this study, a CO₂ photocatalysis reaction is carried out using CO₂ nanobubble as the source of CO₂. This is expected to increase the contact surface area of the gas and liquid phases and increase the CO₂ mass transfer coefficient. Besides, TiO₂ is modified by dispersing it on the CNC surface and adding nitrogen doping. Nitrogen doping is expected to lower the band gap and minimize the electron-hole recombination so that more electrons are utilized for CO₂ reduction, leading to higher CO₂ conversion. The aim of this study is to study the feasibility of CO₂ nanobubble usage in multiphase CO₂ photocatalysis reaction in a batch reactor without the in and out flow of CO₂ gas. We believe that the result of this study can open new possibilities in the development of CO₂ photocatalysis reactions.

2. Methods

2.1. Materials

Titanium tetra isopropoxide (TTIP, 97.0%), ethanol absolute (99.99%), nitric acid (69%), triethylamine, and sodium hydroxide (50%) were purchased from Merck kGaA, Darmstadt, Germany. Cellulose nanocrystals (CNCs) were purchased from Celluforce, Quebec, Canada. Deionized water was used in all experiments.

2.2. Photocatalyst Synthesis

The TiO₂ photocatalyst was synthesized by the sol-gel method under ambient conditions using TTIP as a precursor. While stirred continuously, 1.2 ml of TTIP was mixed with 20 ml of absolute ethanol. 20 mL of Nitric Acid (0.1 M) was added to the mixture and then continued with the addition of 1 g of cellulose nanocrystals (CNCs) under vigorous stirring for 10 minutes. NaOH 0.2 M solution was added dropwise until the mixture reached a pH of 4. The mixture becomes more viscous at this stage and a gradual color change occurs from transparent to white. The mixture was then left for 24 hours to undergo the aging process. After aging, the mixture was centrifuged 3 times at 6000 rpm and finally dried at 70°C for 12 hours. The resulting white solid is referred to as TiO₂/CNCs photocatalyst. To obtain N-TiO₂/CNCs, 0.8 mL of triethylamine (TEA) was added to the mixture prior to the addition of NaOH solution. The synthesis procedure scheme of TiO₂/CNCs and N-TiO₂/CNCs are presented in Figure 1.

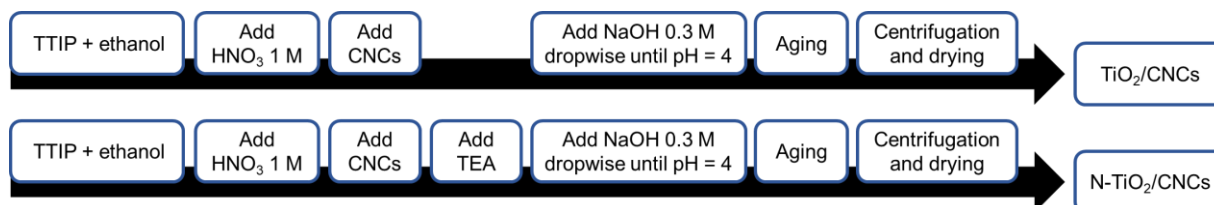


Figure 1 Photocatalyst synthesis procedure

2.3. Photocatalyst Characterization

TiO₂/CNCs and N-TiO₂/CNCs photocatalysts were examined by X-ray diffraction (Bruker D8 Advance, Japan) using Cu K α radiation, with an accelerating voltage of 16 kV and a current of 30 mA. The characteristic peaks of anatase [101] peak at $2\theta = 25^\circ$, brookite [121] at $2\theta = 31^\circ$, and rutile [110] at $2\theta = 27^\circ$, respectively, were used to estimate the crystallite size of the samples. Scanning electron microscopy (SU-3500, Japan) was used to study the morphology of the TiO₂/CNCs powders at a working distance of 8 mm with an

accelerating voltage and current of 30 kV and 100 mA, respectively. High-resolution transmission electron microscopy (HRTEM, H9500, Japan) was used to study the particle size and distribution. UV-Vis diffuse reflectance spectra (DR UV-Vis) of the prepared samples were measured by a UV-Vis spectrophotometer (UV-2600, Shimadzu) with an integrating sphere attachment ranging from 200 to 800 nm, and TiO₂ was used as a reflectance standard. The band gap energy (E_g) for the direct band gap semiconductor was evaluated using the Kubelka-Munk function as presented in Equation 1.

$$f(R_\infty) = \frac{k}{s} = \frac{(1-R)^2}{2R} \quad (1)$$

where $f(R_\infty)$ is the Kubelka-Munk function, k is the absorption coefficient, s is the scattering coefficient, and R is the surface reflectance.

2.4. Nanobubble Generation and Photocatalytic Activity Test

CO₂ nanobubbles were generated by the hydrodynamic cavitation method using a nanobubble generator from Nanobubble.id with the type of NB S1. The according to the system depicted in Figure 2a. During the generating process, the temperature was kept below 28°C. Water was pumped into the main container to create a circulation from the main container to the nanobubble generator and vice versa. The CO₂ gas with 0.1 LPM flow rate was injected into the nanobubble generator via the water that passed through it. After 1 hour of nanobubble generation, the water in the main container was either stored for characterization or utilized in CO₂ photocatalysis. The characterization of nanobubble is carried out by dynamic light scattering (DLS) to analyze nanobubble size and its distribution.

The photocatalytic activity test was carried out in a batch reactor, as illustrated in Figure 2b. The reactor was filled with 200 mL of water containing generated nanobubble and 0.2 g of photocatalyst. The mixture in the reactor was stirred at 300 rpm during the reaction process. The photocatalysis was carried out by irradiating the reactor using a UV lamp (UV-C, 15 W, 280 nm) or visible lamp (15 W, 580–750 nm) on both sides, as illustrated in Figure 2b. The reaction was carried out for 6 hours, and the sample of liquid product was taken to be analyzed using Gas Chromatography with Porapack Q column. All the CO₂ used in this system is sourced exclusively from pre-generated CO₂ nanobubbles. However, there is a drawback to this setup as the product yield is limited due to the finite supply of available CO₂. Nevertheless, this system was intentionally designed to showcase the significance of CO₂ nanobubbles in the photocatalytic conversion of CO₂ into solar fuel.

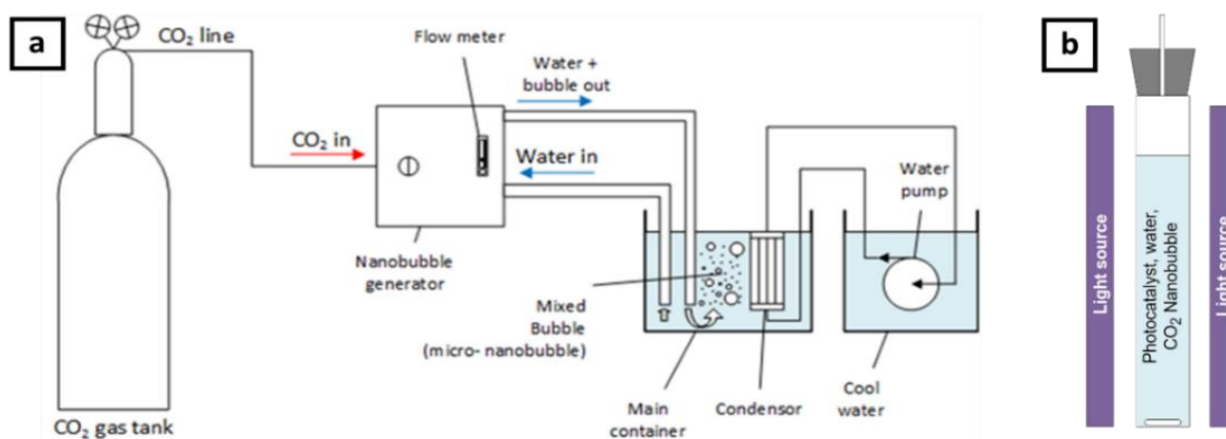


Figure 2 (a) Nanobubble generation system for CO₂ nanobubble generation and (b) CO₂ photocatalysis batch reactor using nanobubble

3. Results and Discussion

3.1. Visual Observation of Photocatalyst Synthesis

TiO₂/CNCs synthesis processes can be separated into four steps: 1) TTIP mixing with solvent, 2) HNO₃ to lower the pH, 3) NaOH addition, and 4) aging. The visual observation of each step is presented in Figure 3.

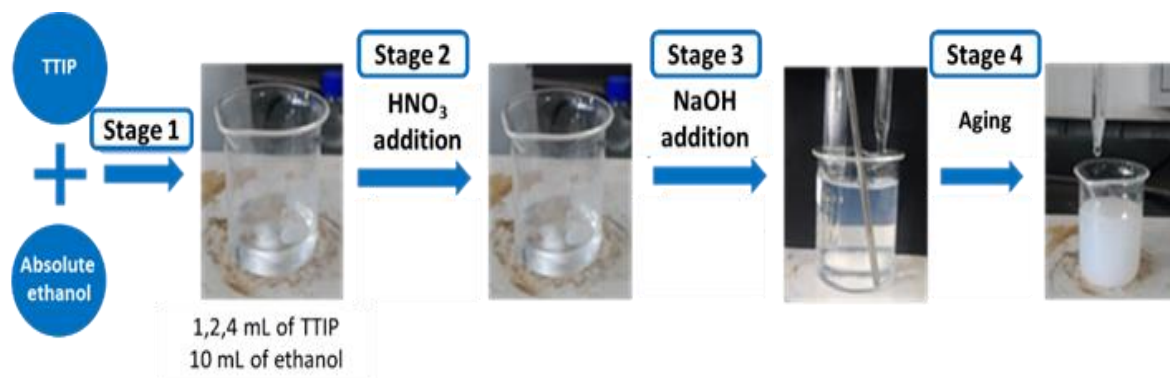


Figure 3 Visual observation of Photocatalyst Synthesis through the sol-gel method

In the first step, TTIP was mixed into absolute ethanol with a purity of 99.99% and followed by HNO₃ 1 M addition to avoid uncontrolled formation of Ti(OH)₄ due to the hygroscopic nature of TTIP. Ti(OH)₄ particles were formed during the hydrolysis of TTIP, which was triggered by the gradual addition of NaOH (Mustapha *et al.*, 2020). The hydrolysis process was then followed by a condensation process that occurred during the aging stage, which took 24 hours. In this stage, the Ti(OH)₄ was converted to TiO₂ while producing water. As reported by Martakov *et al.* (2018), during the aging stage, not only does the formation of TiO₂ occur, but also the deposition of TiO₂ on the surface of the CNCs. The deposition of TiO₂ on the surface of TiO₂ occurs through electrostatic and chemical interaction. The electrostatic interaction is triggered by the positive surface charge on TiO₂ particles and the negative surface charge on the CNCs surface due to the existence of hydroxyl groups. The chemical interaction between TiO₂ and CNCs occurs in the form of hydrogen bonds between TiO₂ and hydroxyl groups on the surface of CNCs.

3.2. Photocatalyst Characterization

Several characterizations were carried out to confirm the presence of TiO₂ on the surface of the CNCs, namely TEM, XRD, and DR UV-Vis. Figure 4 shows the CNCs and TiO₂/CNCs under TEM observation.

TEM characterization results show that CNCs and TiO₂/CNCs have needle-like shapes. The average diameter and length of the CNCs particles are 30.30 ± 7.90 nm and 299 ± 67 nm, respectively, as determined from the analysis results using ImageJ software. Although the CNCs and TiO₂/CNCs particles have a common shape, the two have differences when viewed from the edges. On TiO₂/CNCs, black spots are suspected to be TiO₂ particles attached to the surface of the CNCs. Further confirmation of the presence of TiO₂ can be seen from the results of the XRD characterization, as presented in Figure 4c.

The CNCs sample showed peaks of 2θ at 15°, 17°, 23°, and 34°, which indicated that the cellulose contained in the CNCs was type I cellulose. In detail, each of these peaks successively represents the crystallographic plane of (1 0 1), (1 0 -1), (0 0 2), and (0 0 4) (Jiang *et al.*, 2017). Meanwhile, the TiO₂ sample showed 2θ peaks at 24.9°, 37.6°, 47.8°, 53.7°, 62.5°, 68.5°, 70.1° and 74.88° which represents the crystallographic plane of (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 0 4), (1 1 6), (2 2 0) and (2 1 5). These peaks are in good agreement with anatase TiO₂ peaks based on JCPDS no. 21-1272.

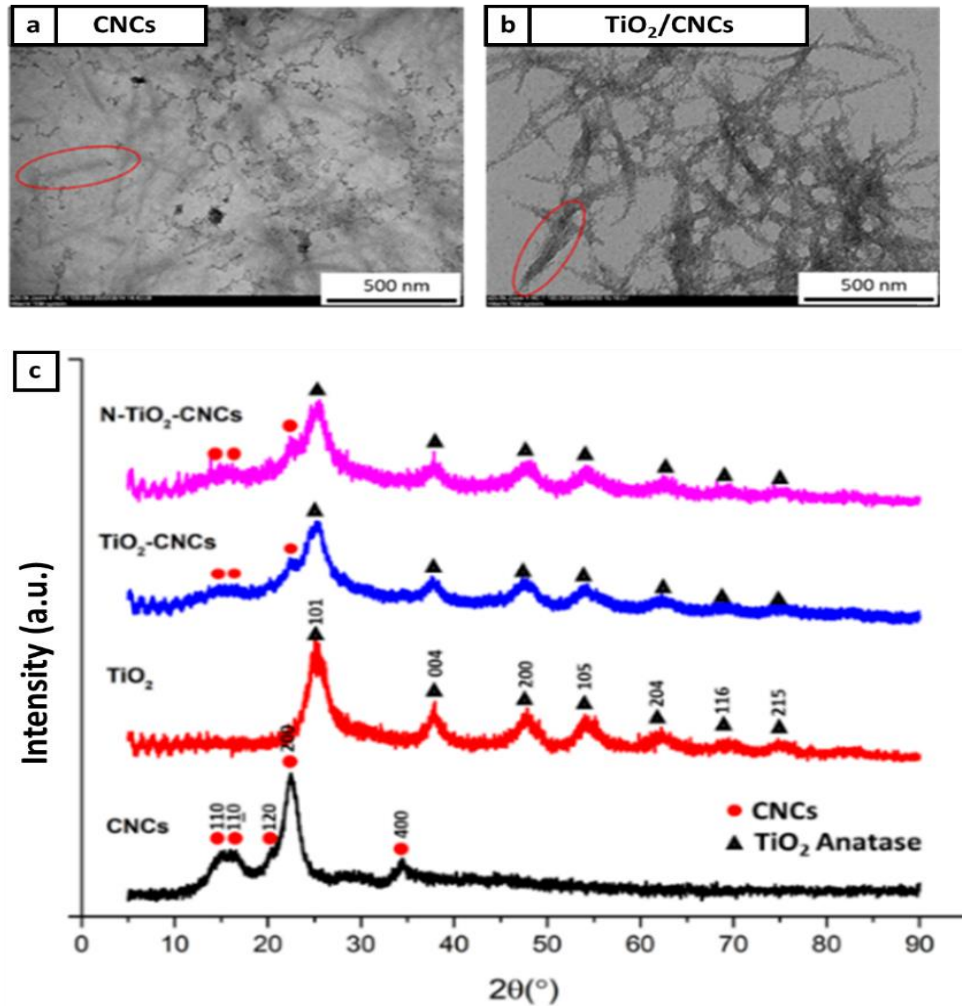


Figure 4 (a,b) TEM observations and (c) XRD curve of CNCs and TiO₂/CNCs

DR UV-Vis is another method that can confirm the presence of TiO₂ and estimate the band gap of the photocatalyst. Figure 5 shows the results of the reflectance curves and Kubelka-Munk Plot of CNCs, TiO₂, and TiO₂/CNCs.

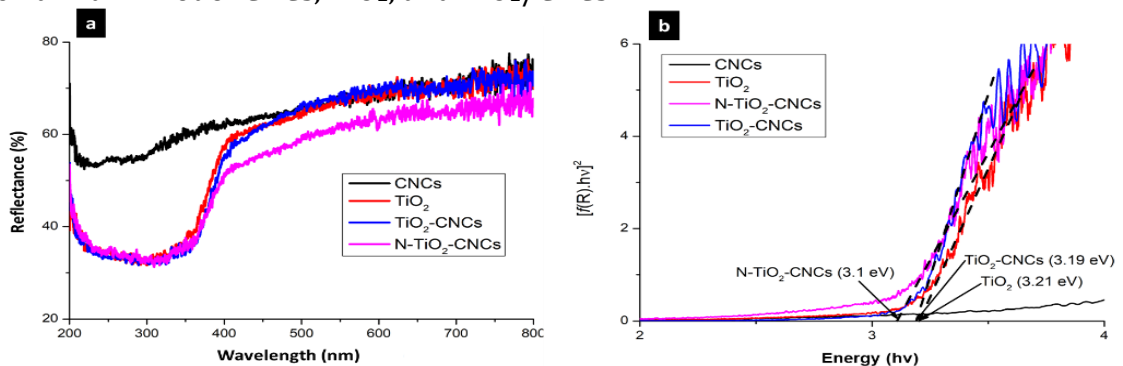


Figure 5 (a) Reflectance curve and (b) Kubelka-Munk Plot of CNCs, TiO₂, TiO₂/CNCs, and N-TiO₂/CNCs

As depicted in Figure 5, CNCs exhibit a relatively straight reflectance curve, suggesting that there is no dominant light absorption activity at a specific wavelength. This is expected since CNCs are not semiconductor materials capable of exciting electrons when exposed to light at a particular wavelength. In contrast, TiO₂ and TiO₂/CNCs have a lower reflectance at a 200–400 nm wavelength, meaning that more light is absorbed in that area. In other

words, TiO₂ and TiO₂/CNCs can excite electrons in irradiating light with a wavelength below 400 nm. This wavelength is equivalent to a band gap energy of ~3.2 eV, which is the band gap of TiO₂ (Mustapha *et al.*, 2020). From Kubelka-Munk Plot, the TiO₂ and TiO₂/CNCs samples have a band gap of 3.21 and 3.19 eV, respectively. The N-TiO₂/CNCs photocatalyst has a band gap of 3.1 eV, which is lower than TiO₂/CNCs. This result confirms that nitrogen doping can lower the band gap energy and enable the photocatalyst to be used under visible light irradiation.

3.3. Nanobubble Characterization

Figure 6 shows the visual observation of the water before and after the nanobubble generation.

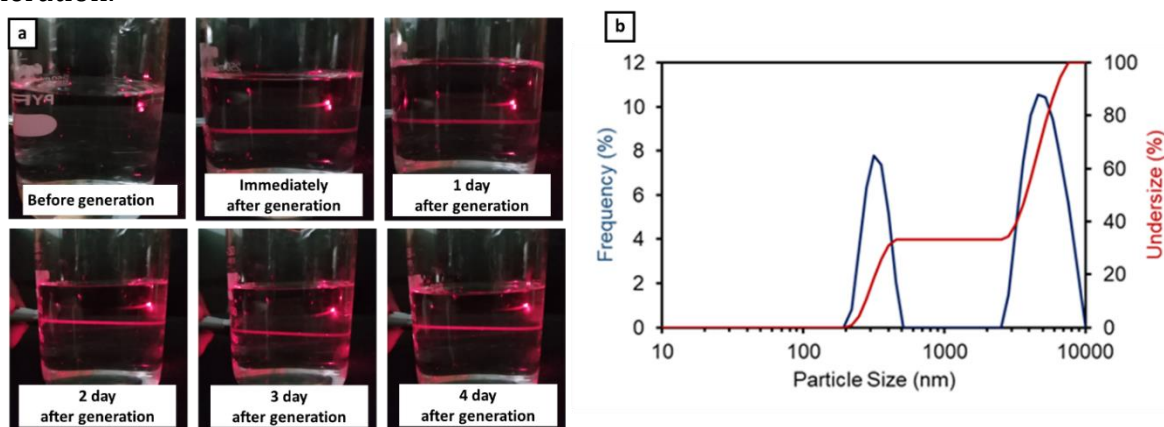


Figure 6 Nanobubble characterization results: (a) Visual observation; (b) Dynamic Light Scattering (DLS) result

Nanobubble has high stability because it has a very long rising time. In comparison, the rising time of nanobubble particles can be days or even months (Ulatowski *et al.*, 2019), while microbubbles and macrobubbles, respectively, have rising times in the range of minutes and seconds (Temesgen *et al.*, 2017). Figure 6a shows that CO₂ nanobubble still remained in the water after 4 days, which is an important justification for the usage of CO₂ nanobubble in batch reactors after its generation. According to the DLS results in Figure 6b, the generated CO₂ nanobubbles exhibit two size clusters, categorized as nanobubbles with a size of 200–400 nm and microbubbles with a size of 2–10 μm. Based on the plot of undersize (y-axis on the right) vs particle size, 35% of the total generated nanobubbles are below 400 nm in size.

3.4. Photocatalyst Activity Test of TiO₂/CNCs

The photocatalytic activity test was carried out at room temperature with a UV-C lamp and visible light in a batch reactor for 6 hours. Figure 7 shows the GC curve of the liquid product resulting from CO₂ photocatalysis with TiO₂/CNCs photocatalyst.

Based on Figure 7a, the liquid product of CO₂ photocatalysis has two peaks at 1.1 and 2 minutes, which are the retention times for water and methanol, respectively. In detail, the resulting methanol product was 0.77 mmol/g catalyst for TiO₂/CNCs and 1.13 mmol/g catalyst for N-TiO₂/CNCs. The existence of methanol in CO₂ photocatalysis products at least proves two things. First, TiO₂/CNCs and N-TiO₂/CNCs photocatalyst has photocatalytic activity under UV-C light, so the photocatalysis reaction can occur. Second, the proposed system using CO₂ nanobubble is feasible for CO₂ photocatalysis in multiphase reactions. An important point to highlight from this result is that there was no CO₂ gas flow during the photocatalysis reaction. All CO₂ utilized during the reaction solely originated from CO₂ nanobubbles pre-existing in the system before the reaction.

Figure 7b shows the comparison of TiO₂/CNCs (undoped) and N-TiO₂/CNCs (N-doped) photocatalysts under visible light irradiation. It is shown that the doped photocatalyst exhibits visible light photocatalytic activity while the undoped does not. This is due to the lower band gap energy of N-TiO₂/CNCs, so visible light with lower energy can excite the electron in the doped photocatalyst. From the Kubelka-Munk Plot that has been discussed earlier, N-TiO₂/CNCs have a band gap of 3.1 eV. Based on the Planck equation ($E \text{ (eV)} = 1240/\lambda \text{ (nm)}$), 3.1 eV is equivalent to the wavelength of 400 nm, which belongs to visible light. In comparison, Kumar, Das, and Deepa (2020) reported that nitrogen doping addition to TiO₂/CdS can reduce the band gap from 3.17 eV to 2.91 eV (Kumar, Das, and Deepa, 2020).

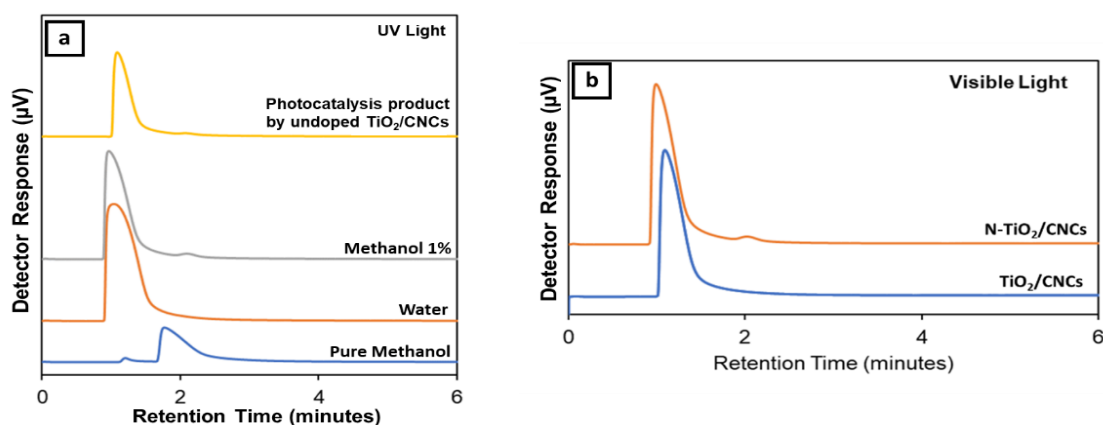


Figure 7 GC curve of liquid product produced from CO₂ photocatalysis by TiO₂/CNCs photocatalyst at (a) UV-C light and (b) visible light

4. Conclusions

In this study, the photocatalysis reaction of CO₂ was carried out in a batch reactor, where CO₂ gas in the form of nanobubbles in water was directly irradiated with light. There is no flow of CO₂ gas in and out. All CO₂ used for the reaction was provided from nanobubbles in the water. The presence of methanol in the photocatalysis product with this system proves the feasibility of multiphase systems with CO₂ nanobubbles for CO₂ photocatalytic reactions. Nitrogen doping to the photocatalyst reduced the band gap from 3.20 eV to 3.10 eV, which was later proven by the photocatalytic activity of N-TiO₂/CNCs under visible light irradiation.

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