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Exploring the Photocatalytic Potential of TiO2 Nanoparticles: A Comprehensive Review

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Abstract - As for the replenishing resource power and pollution removing approach, one of the most potential potentials is the photo-catalytic photo activation of CO2 into solar fuels accompanied by semiconductor photocatalysts. Pursuing efficient photoreduction of CO2 to useful products and the development of new photocatalysts are two challenges humanity must overcome in the twenty-first century. Recently, TNTs have been considered in detail because of their possible application in the chemical industry for photovoltaic conversion of carbon dioxide (CO2) into valuable chemicals. Over a period, the change in increasing rate of CO_2 emissions, researchers are now directing their work into raising the rate of CO_2 photoreduction by tuning the TNTs appropriately. A balance on present findings of synthesis and modification process and capacity of TNTs to produce value added products from CO2 is mandatory to paint its potential usage. From this analysis, the state of the art in current TNT manufacturing technologies, available strategies for modifying the surface of CO2 to enhance TNT photoreduction, and major findings of prior research can be derived to determine the future directions for research and possible challenges. Some of the challenges that need to be addressed in the CO2 to useful products photoreduction process include; the photocatalyst stability, reusability of the TNT photocatalysts, and its visible light performance. Besides, decision-making on the choice of optimal modification procedures is critical. Thus, photocatalytic reactions with TNTs can be improved by overcoming the abovementioned drawbacks and using the present photoreactor model that makes the best of photocatalysts, as well as the partial pressure of the reactants and incident light.

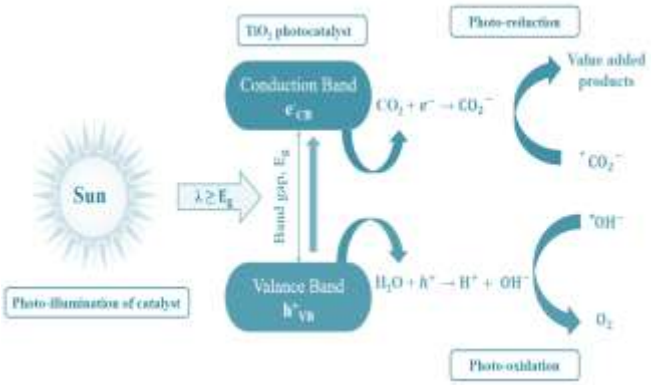
Key Words: Photocatalysts, CO_2 photoreduction, TNTs (Titanium Dioxide Nanotubes), Semiconductor photocatalysts, Solar fuels, Visible light performance

1.INTRODUCTION *(Size 11, Times New roman)*

Change is good, but it needs to be done in a gradual manner that will not hamper the next generations. The current literature has paid a lot of emphasis on the variable impacts and contributions of carbon dioxide (CO2) to ecosystems. An imbalance within the amount of energy that reaches the earth is produced by an increase of the amount of CO2 within the atmosphere, resulting in a rise in earth temperature [1]. There has been a dramatic increase in carbon dioxide emissions, and the causes are well-known: rapid industrial growth, increase in use and consumption of fossil fuels, and large scale deforestation [2]. They suggest that the global temperature increase to a level of 1 ◦C by 2049 due to continuous adherence to the current trends concerning the concentrations of CO2, which is projected to be 460 ppm. Some strategies that need to be incorporated in an attempt to readdress the issue of climate change include: the utilization of renewable energy resources, the efficient use of energy and reduction and utilization of carbon dioxide (CO2).

There has been increase in the conversion and utilization of CO2 in the recent years in the following ways. Besides being a realistic plan of controlling CO2 emissions, artificial photosynthesis can generate molecules with additional worth utilizing the solar energy [3]. Since it is able to address the demand for green fuel for transportation while at the same time re-utilizing atmospheric CO2 through direct conversion of sunlight, it is one of the most promising approaches. Due to its coefficient to photactivity, its high durability, non-toxicity and relatively low cost, TiO2 was used as a photocatalyst to effectively lower the level of CO2 during the photosynthesis [4]. As depicted in Figure 1, the amount of CO2 which is photoreduced when employing TiO2 as the photocatalyst. Nonetheless, TiO2 exhibits a low efficiency of solar light absorption that falls around 4% and the fast recombination of photogenerated charges as well as a comparatively wide inherent band gap (Eg = 3. 3 eV for anatase). Therefore, it is possible to conclude that TiO2 modification is necessary to apply these photocatalysts in real-life practices.

Fig. 1: Illustration of the mechanism of TiO2 based photocatalysts



for the CO2 reduction process.

Therefore, phase modification is an approach used to enhance the photocatalytic performance of TiO2. Among all the 1D TiO2 nanostructured materials, the TiO2 nanotubes (TNTs) electrochemically synthesized have received much attention because of the following reasons; cheap synthesis technique, possible photo catalytic properties, large surface area to volume ratio [5]. As indicated in figure 2, the application of TNTs in photocatalytic CO2 reduction was rapidly rising in the last couple of years. TNT photocatalysts have been widely applied in reduction of carbon dioxide emissions overly since their first use in 2009. Subsequent studies to enhance photocatalytic CO2 reduction of TNTs included doping, sensitization, and heterojunction modification. Thus, in an effort to indicate further directions in the present study, it is necessary to review the information on TNTs concerning their influence on the reduction of CO2.

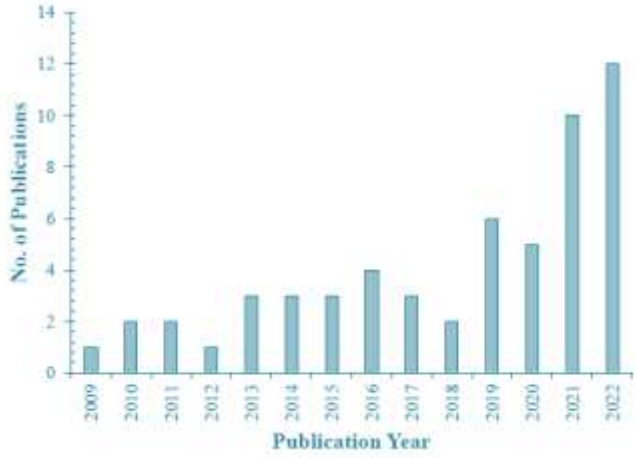


Fig 2: The number of papers identified within the search term "TiO2 nanotube and photocatalytic CO2 reduction" using Scopus search on September 5, 2022.

2. OVERVIEW

First of all, there are several types of gases that affect climate change, but the most captivating and dangerous one is CO2. Increase of carbon dioxide emissions is one of the greatest threats of the world and it is currently a hot issue [6]. Reducing anthropogenic CO2 emissions AND capturing and converting the resultant CO2 emissions into beneficial products are two instrumental steps for preserving the environment. In this regard, the use of a photocatalytic process to transform CO2 into added value products can be considered a potential approach. Carbon dioxide in gaseous state can be converted to hydrocarbons (methane, ethylene, and ethane) and oxygenated hydrocarbons (methanol, ethanol, formaldehyde, formic acid, acetic acid) based on the photocatalytic activities along with huge energy intensity. Generally, CO is known to exhibit the highest emphasis on intermediate product during the photo reduction of CO2. Another challenge that stands in the way of CO2 photoreduction in general is the issue of product distinction. This therefore means that attempts to enhance the photocatalytic CO2 reduction rate is of later interest through the use of TiO2 based photocatalysts. For example, under the current situation, the rising review activities as well as original research works are also being conducted to offer the current situation to scientific organizations. From the reviews that compared and discussed the photocatalytic CO2 reduction process where TiO2 is used to produce CH4 or some other valuable components, none of them addressed the concept exclusively with regard to TNTs despite several articles being available in the literature [7]. Therefore, to improve the photocatalytic CO2 sorption and reduction process to high-valued products while using TNTs, this study focused on the following goals. Scientific reports of the novel particles for the CO2 photo reduction enhanced by TNTs or modified TNTs are presented here. The special audiences who could benefit from the present article, therefore, are the scientist interested in the state of the art of the TNT based photocatalytic CO2 conversion to high value added products.

3. FUNDAMENTALS

Photostability of titania, its non-toxicity, availability and photocatalytic properties have made it a widely known and studied photocatalyst in the last two decades. The four common polymorphs of titanium dioxide that exist under normal environmental conditions are anatase, rutile, brookite, and TiO2(B). For instance, the existing literature shows that anatase TiO2 is more photocatalytically active than rutile or brookite TiO2. Hence, anatase is considered to be the most suitable among these forms for the CO2 photoreduction at the nanoscale level due to its faster charge carrier separation, higher kinetic stability, lower surface energy and the proper bandgap energy. Thus, the Dsorbitol and other sugar alcohols enable one to change the crystal structures of the TiO2 nanoparticles. Some of the forms of pure TiO2 which may be altered to increase its photocatalytic activities include the nanoparticles, 1D nanofibers, 2D nanowires, nanorods, and 3D nanoflowers (Figure 3). The additional inner shells of the nanotube shape make it have more surface area compared to the other one dimensional TiO2 forms. Still, it is possible to further modify the TNTs on their internal and external walls. For the edification of its photocatalytic applications, photons may undergo multiple reflections within the TNT hollow structure. As it is commonly understood, the photoconversion efficiency increases as the diffusion length of the materials increases. The organization of the TNT photocatalyst and the strength of the bonding of the composites enhance the charge transfer. Worldwide, TiO2 nanotubes are considered suitable for photocatalytic CO2 reduction due to the following factors; they are non-toxic, chemically and thermally stable, possess a high surface area and low recombination rates [8].

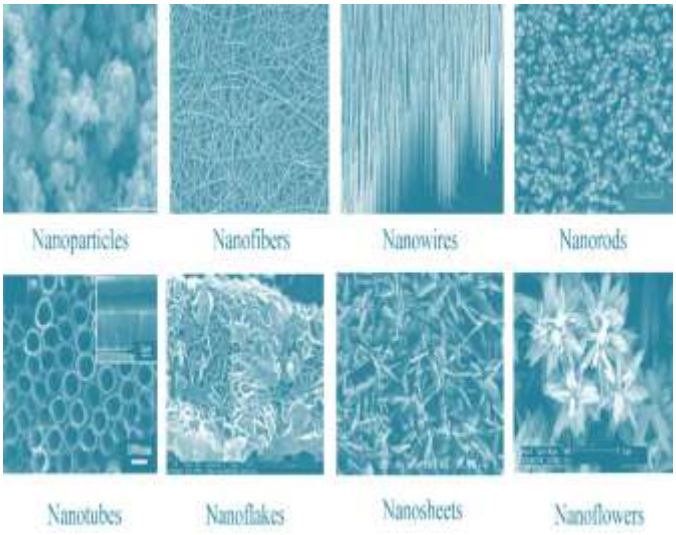


Fig. 3: reveal the presence of many TiO2 hierarchical nanostructures.

4. SYNTHESIS

As it is in one dimension, which is arranged in a tubular structure and has many applications, the TiO2 nanotube (TNT) has become a popular research focus. Here again, activation/diffusion governed photocatalysis unveils that TiO2 nanotubes are synthesized as superior photocatalysts to other 1D nano structures with high catalytic activity. There are several methods of synthesizing TNTs, the main of which are: electrochemical anodization, hydrothermal treatment, template synthesis, sol-gel, etc. Some of the anodization techniques allow the formation of self-constructed TiO2 nanotube array structures

through the change of the basic geometrical factors such as length capability, diameter, and wall thickness [9]. In this work, the target morphological structures have been synthesised by influencing the electrolyte types, concentration, pH, temperature, anodization voltage, time and electrode type. Several methods of TNT formation have been discovered, but the one depicted in figure 4 uses electrochemical anodization. The method of generating TNTs includes the following steps: On the application of a potential at an electrode applying on Ti substrate, an oxide layer is produced. Next, the fluoride ions amalgaume with this layer causing the formation of TiF or TiF62- which dissolve in the electrolyte. At the same time, the oxidation layer expands to the substrate that forms a comparably heterogeneous layer with brief anodization. The longer the anodization time, the inner surface of the layer is dissolved out, to form the ordered tubes with the proper length and diameter.

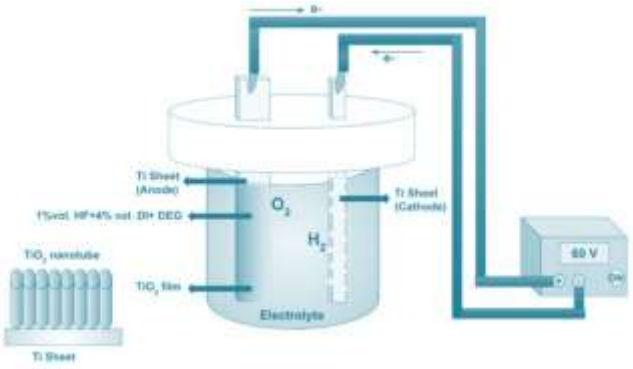


Fig 4. Process of the electrochemical anodization, which is used in the formation of TNTs is outlined below.

It has been evidenced from above experiment that both the sol-gel and hydrothermal synthesis routes for preparing TNTs are randomly oriented. In contrast, electrochemical anodization results in the formation of TNTs that are aligned vertically and possess an average length, thus increasing the charging transfer rate. The limitations associated with the use of template helper strategy that directly determines the morphology of the nanotube to the geometry of the employed template make the anodization method ideal. This technology is often applied because the technology is easily controlled, offers high adhesion, can be conformably constructed to certain particular applications, and may be reduced to measure the necessary dimensions.

5. PHOTOCATALYTIC CO_2 REDUCTION

Photocatalytic CO2 reduction which is a new approach for reduction of CO2 emissions and at the same time providing renewable and sustainable energy sources for the world has been identified as an emerging technology. In particular, it has a linear and symmetrical arrangement, fully oxidized carbon, and a GCE up to 798 for carbons. 6 kJ mol−1 at 254 K; The stability of CO2 is very high because its Gibbs free energy change is -330 kJ mol−nage. Hence, a photocatalyst or energy input is compulsory in order to convert it to compounds with added value. When the energy band gap of the photocatalyst is irradiated with photons > mv, the electrons (e−) are promoted from the valence band (VB) to the conduction band (CB) leaving behind no holes (h+) in the VB. next that, a portion of the e−/h+ couples immediately recombine and do not participate in the next redox reactions and the energy is partially dissipated and converted into heat. The surface of the photocatalyst is made to act as a place of reduction and oxidation where the other electrons and holes are utilized. There are many factors that make photocatalytic reaction mechanisms for photocatalytic reduction of CO2 quite complex; these include activation and adsorption of CO2 molecules, product selectivity, and high energy barriers.

The study shows that depending on which reductans is used, CO2 undergoes distinct chemical pathways for photoreduction. Figure 5 illustrates the two most recognized and justified methods known to convert CO2 to CH4. These are the formaldehyde leading to carbene pathway. To start a reduction pathway, one electron must be transferred from the photocatalyst's CB to capture an electron to form a CO2− anion radical. The blue arrows in Figure 5 indicate several potential intermediates of the formaldehyde route that is capable of converting CO2 to CH4. The carbon dioxide to methane reaction is carried out through carbene pathways, which include initial deoxygenation followed by hydrogenation.

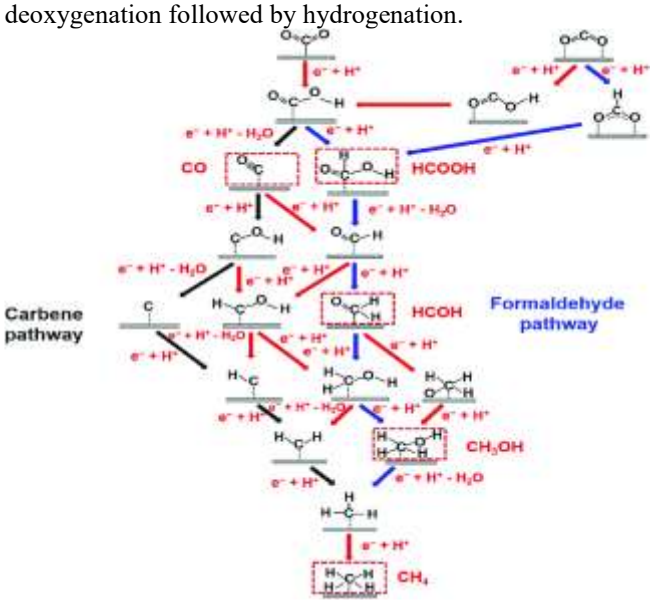


Fig. 5 taken from [10], there are the possible pathways for photocatalytic CO2 reduction on the photocatalyst surface to generate CH4 or other hydrocarbon fuels.

6. PHOTOCATALYTIC CO_2 REDUCTION

Due to such a favorable morphology that allows the most favorable dispersion of photocatalytic reduction products and relatively low recombination rate, practical application of TiO2 in nanotube arrays is highly desirable [11]. It is concluded that crystal shape, wall thickness, length of nanotube, and diameter greatly influence the photocatalytic activity of TNT photocatalysts. For instance, the rate of the photocatalytic CO2 reduction in multi-walled TNTs was twice as fast as that in single-walled TNTs for CH4 production and 4 times greater for CH3OH production. When the structure defects such as oxygen vacancies and surface defects are present in the photocatalysts, the photoactivity is improved. The TNTA, or synthetic black TiO2 nanotube arrays, and the photoactivity of the material. Thus, under visible light irradiation, black TNTA synthesized 179. As low as 46 mol g1 h−1, sanctioning highly efficient CO2 photoreduction to CO. It is owing to it that the development of photoinduced charge, interfacial charge transit, and interfacial reaction were significantly improved, making this possible.

A number of parameters influence the CO2 photoreduction that comprises the light intensity on the reactant, the temperature of the process, and the photocatalytic reactor's partial pressure of the reactant . Evaluation of TiO2 nanotube arrays the photocatalytic activity under various conditions, sunshine and partial pressures of water and carbon dioxide. Under conditions of a 390:A CO 2 /sunlight ratio of 1 and a 0. At a 6 MPa CO2 pressure the findings revealed that the photocatalytic efficiency of TNTA was one hundred times that of pure TiO2. The alternative ways have been employed by researchers to improve the performance of TNTs when used as a single photocatalyst. Hereby, there are no modification processes in the assessment of amorphous TNTA photocatalytic CO2 reduction with the CH4 reaction rate of 13. 0. Producing 145. 5 µmol g−1 h−1 of CH4, flame-annealed TNTs synthesized in an aqueous electrolyte solution exposed to visible light exhibited higher photocatalytic activity compared with those synthesized in an organic electrolyte solution. This method made it possible in the synthesis of a self-doped TNT photocatalyst without the support of the electrolyte as well as counter electrode. The maximum conversion efficiencies of CO2 to CH4 by using self-doped TNTs were 655 percent. 3µmol g−1 h−1and for C2H6, the maximum reaction rates were 51. 5 µmol g−1 h−1. This gives us a clear indication that the electric-assisted method is much more effective than traditional photocatalysis by a ratio of about 3 to 1.

7. KINETIC MODELLING

When it comes specifically to CO2 photoreduction, the kinetic model, as represented by the series of reactions sketched above, is not the focus of nearly as much attention as might have been expected [`1]. All the photocatalyst surface's active sites are equally accessible to the reactant, which is why an intrinsic model comes in handy since it tells the kinetics of the whole process, and it is not scale dependent. In order to quantify the rate of the CO2 photoreduction one may applied empirical models along with in situ experiments, and a microkinetic approach. As for the reaction kinetics and the rates of reactants and products which are in equilibrium at photocatalyst interfaces, heterogeneous photocatalysis employs kinetics equations. In many cases the kinetic parameters involve the reaction rate constant, and the constant of adsorption equilibrium. In the photocatalytic reactor, there are five main processes that usually occur and they will be discussed in details in next section as shown in figure 6. This step entails combining the reactants with the reactor, and for this reason, both water and carbon dioxide will be expected to diffuse to the photocatalyst surface. The second process is the diffusion of the reactants on the surface there being the active sites. The third step is to furnish the requisite energy for the reaction. The fourth step is the actual chemical process of interaction between two neighboring active sites in the presence of light. The last process is the rinsing of the products off the surface of the photocatalyst. The details of CO2 photoreduction rate over TiO2 photocatalyst using computational fluidynamics and Sips model. TNT photocatalysts are still untapped in the computational modeling area for further research. In order to evaluate the assumptions utilized for the empirical kinetic studies based on the efficiency of the photocatalyst, it is essential to identify the molecular processes happening at the photocatalyst surface. Another more promising approach is understanding the CO2 photoreduction activities on photocatalyst surfaces by employing in-situ analytical techniques. Some in-situ spectroscopy tools like photoluminescence PL, X-ray photoelectron spectroscopy XPS as well as Fourier Transform Raman Infrared spectroscopy FTIR are highly essential in analysing CO2 photoreduction.

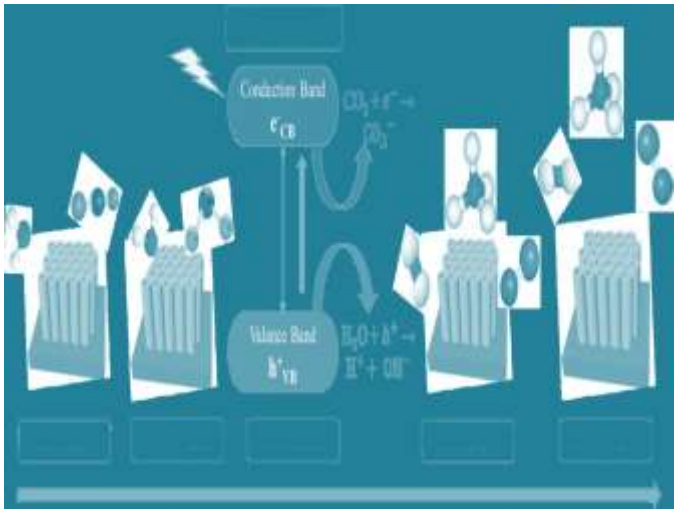


Fig 6: Potential processes in a photoreactor for the photoreduction of carbon dioxide.

As lacking the quantification of heat and mass transfer effects, microkinetics is the investigation into the fundamental molecular events that take place on photocatalyst surfaces. Here, I give one such practical method which may be employed to explore the options for enhancing the rate of CO2 photoreduction further: microkinetic analysis. This method develops models which can filter the photocatalyst database and assist in designing new photocatalysts, which is a great benefit because the process can be time-consuming and costly if done manually in a lab. As another approach rather less popular than microkinetic modeling, scientifically sound LH kinetic models have been worked out. The essence of this approach can be credited for the consideration of partial pressures and irradiation effects in the kinetic data, which is a plus. One possible drawback is the efforts and time required for acquiring kinetic data of the CO2 photoreduction process. In the non-homogeneous photocatalytic method, the rate of the reaction tends to be measured in relation to the extent of adsorption of the final products on the surface of the photocatalyst after the reaction. And, one of the photocatalytic activity measures used by this method is the rate of reaction which is determined by the number of moles of the reaction in a particular period and area. As you are aware there is this common belief that the surface reactions need the longest time and are responsible for the rate of the reaction. For such reactions, L-H mechanism can be applied only when both the reactants are adsorbed to the adsorbent surface and to different extents.

8. CONCLUSION AND FUTURE WORK

A possible application of TiO2 nanotubes as a photocatalyst is the conversion of solar energy to power in the form of flammable gases via reacting with carbon dioxide. The nucleation and growth of TiO2 nanotubes can be achieved simply through the anodization process, which makes it possible to fabricate TiO2 nanotubes of different forms and dimensional parameters. This particular piece of analysis focuses on two factors- the amount of progress that has made in the previous decade in TNT application in the process of CO2 photoreduction. It is also described in this

paper a number of kinetic approaches that have been derived to estimate rate kinetics of CO2 photoreduction. Overall, the application of raw or modified TNTs in decreasing CO2 has been impressive depending on the kind and extent used. CO2 changed into CH4 using focal photovoltaic effect when utilizing TiO2 nanotube photocatalysts with consisted of focused sunshine to enhance the impact light thickness and warmth temperature with the reaction. Among all the nanocomposites prepared ZnO-Au-TNT Z-scheme heterojunction has the higher CO2 reduction efficiency and CH3OH yield 6%. Similarly, in the case of modified TNTs, the highest value of 69mmol g−1 h−1 for the perceived TC was observed. Among all the carbon-loaded electrodes, the TNTs with GQD modification exhibited a 4-fold enhancement in photocatalytic CO2 reduction compared to virgin TNTs. 9. The rate of reaction emanating from photocatalytic CO2 reduction to value added products is most often expressed in terms of the rate constant, which is arrived at via the use of the LH model.

In the case of photocatalytic CO2 reduction, there have already been many investigations; however, the low selectivity of the product has not reached a stage that it can be used in an application. Yet, there are various issues that need to be addressed before these technologies will be tightly applied to different industries, as the majority of experiments were made in laboratories. In further improving the performance of TNT photocatalysts, some challenges should be addressed; they include: the problem of charge-carrier recombination, the issue of visible light activation, the issue of fast charge separation, the problem of removing TNTs from the substrates, the problem of the utilization of the full surface area of the photocatalyst in the photoreactor, and the problem of modifying the surface of TNT photocatalysts in a cost. In order to catalyse the process of photoreduction of CO2 at a larger scale, what is required is photocatalysts that are stable and recyclable, highly efficient and cost effective and photocatalysts which provide better kinetic descriptions. However, prior research has not devoted adequate attention to them. They suggest that further studies should be conducted on the photoreactor design, kinetic analysis, implementation of photocatalysis at the pilot scale, as well as the synthesis of photocatalysts that are inexpensive, highly effective, and reusable.

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