

Critical Review on Modification of TiO₂ for the Reduction of CO₂

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Review Article

Received date: 27/06/2018;

Accepted date: 20/07/2018;

Published date: 01/08/2018

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Keywords: TiO₂, CO₂, Reduction, Photocatalyst, Doping

ABSTRACT

With the passage of time the consumption of fossil fuels is increasing which causes to eliminate more and more greenhouse gases such CO₂ in our atmosphere. CO₂ is much harmful for us causes energy Crises etc. One of the best solution to reduce the quantity of CO₂ into valuable sources such as CH₄, HCO₂H, CH₂O, and CH₃OH by preparing metal oxide semiconducting materials with the use of metal doping and coupling with other metal oxides. Metal oxide (TiO₂) has been used for the photo catalytically reduction of CO₂ due its non-toxicity, cheapness and environmentally friendly. Modification of TiO₂ has concerned many interests due to maximum light absorption, decrease recombination rate, increase surface area to volume ratio, increase CO₂ adsorption ability and enhanced activity of TiO₂ for the conversion of CO₂ into valuable sources. In this review paper, recent work on TiO₂ has been presented including doping of metals and non-metals, coupling with metal oxides and heterojunction composites.

INTRODUCTION

Two main issues of modern world are energy and environment which require great urgent attention. Our planet is facing severe environmental calamities' environmental problems are piling up day by day around us. Our environment is warming up due to increase of global warming with the passage of time^[1,2]. Emission of CO₂ is increasing in planet which causes to enhance global warming^[3]. Our problem of environmental energy crises is solved by the conversion of CO₂ into useful fuel by using TiO₂ nanocomposites. In 1972 First of all Honda and Fujishima discovered photoelectrochemical water splitting by using TiO₂ semiconducting electrodes which was found helpful to meet future energy crisis problems^[4]. Except water splitting into hydrogen and oxygen, photovoltaically conversion of CO₂ into valuable fuel by using metal oxide (TiO₂) semiconducting photocatalysts as a primary requirement which also deal with our environmental energy crisis issues^[5-9].

Photo catalytically conversion of CO₂ into solar fuels such as methane, methanol (CH₃OH), HCO₂H, CH₂O, etc. and water splitting (H₂O) into hydrogen and oxygen have been extensively studied^[10]. Photo catalytical reactor is the best way which is used for the conversion of CO₂ into valuable fuels. There are many metal oxide materials which have been used as photocatalysts under ultraviolet visible irradiations such as ZnO, ZrO₂, Ga₂O₃, WO₃, MgO, CaO, and Al₂O₃^[11-14]. Furthermore, photocatalytic reduction of CO₂ which also have been done by metal sulfides such as ZnS^[15-17] CdS^[10,15,18] and Bi₂S₃^[19]. In addition, other polyoxometalates (CaFe₂O₄) and semiconductors such as GaP or SiC which have also been utilized as a photocatalysts for the reduction of CO₂ in our environment under UV Visible irradiations^[20,21]. In fact, the efficiency of all these photocatalysts is poor which is due to minimum solar light absorption on the surface in the visible region of electromagnetic spectrum^[22] and charge separation is inefficient due to recombination of charge carriers^[23-26]. Anatase TiO₂ has been proved extremely good semiconducting photocatalyst for the conversion of CO₂

into useful hydrocarbons due to its properties such as non-toxicity, chemical stability and photocatalytic activity [27]. Though, TiO₂ semiconducting material is not actively available for visible light irradiation due to large bandgap (3.0~3.2 eV) and approximately only 5% solar light is utilized for the photocatalytic reaction on the surface of TiO₂ [28-30]. There are many efforts which have been done to eliminate this problem and further for its development [31].

In the past, numerous p-type semiconducting materials have been utilized for the modification of n-type TiO₂ to increase the visible light absorption by the formation of p-n heterojunctions [6,32-35]. Visible light absorption is maximum due to narrow bandgap of semiconductors and recombination of charge carriers (e⁻/h⁺) pairs decrease due to visible light absorption. Solar cells which are made by II B -VI A semiconductors such as Hg, Cd, Hg and Te, Se, S, Po have been proved more efficient catalysts for the photovoltaic conversion of solar energy into useful fuels due to maximum absorption rate and minimum material usage [36-39]. For water (H₂O) splitting using electrodeposition method a p-type semiconductor Zinc telluride (ZnTe) has been deposited on TiO₂ semiconducting material [27]. Zinc telluride (ZnTe) is usually used as a photocatalysts due to narrow bandgap. Zinc telluride (ZnTe) enhanced the photocatalytic activity of many materials forming heterojunctions [18,40-42].

There are many approaches widely used for the surface modification of TiO₂ such as impurity doping, metal deposition, Alkali modification, Heterojunction construction and carbon based material loadings for the photocatalytic reduction of CO₂ into useful hydrocarbons [18,43-45]. The main objective of this review paper is to sum up the previous research work on the surface modification of TiO₂ for more efficient efficiency of CO₂ reduction. Finally, conclusion and future outlook of surface modified TiO₂ semiconductor photocatalysts are examined.

MECHANISM PHOTOCATALYTICALLY FOR CO₂ REDUCTION

There are main three steps used for the reduction of CO₂ into valuable hydrocarbons with water (H₂O) as shown in Figures 1-3. Firstly, when we irradiate appropriate light with energy equal or greater than the band gap energy of semiconductor then generation of electron hole pairs take place. Secondly, these produced electrons and holes shift towards the surface of co-catalyst which have contact with semiconductor or semiconductor photocatalysts. Because of recombination of e⁻/h⁺ pairs together the emission of energy in the form of heat take place. Thirdly, the reduction of CO₂ causes due to photogenerated electrons by the adsorption on catalyst surface into CO, HCOOH, CH₃OH or CH₄. Where oxidation of H₂O into O₂ due to holes occurs. In splitting of H₂O into O₂ the first and second steps plays the same role. The recombination of charge is much faster (~10⁻⁹ s) process as compared to the process of reaction (~10⁻³-10⁻⁸ s).

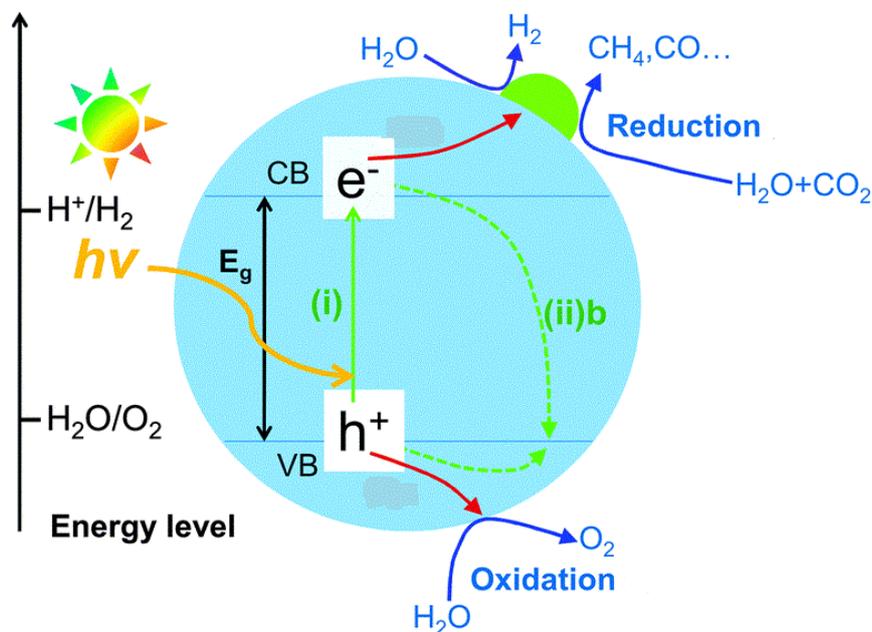
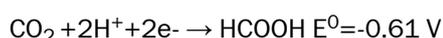
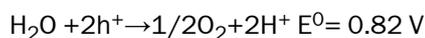
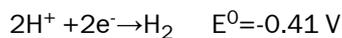
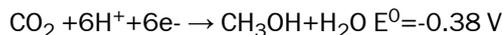


Figure 1. Schematically Basic mechanism of photo catalytically reduction of CO₂ with H₂O on a semiconductor photocatalysts (TiO₂).

Several possible redox potentials and reactions related to reduction of CO₂ summarized below in which useful hydrocarbons such as CO, CH₄, CH₃OH, HCOOH and HCHO are all required products.

[E⁰ (V) vs. NHE (pH=7)]





During photo catalytically CO_2 reduction reaction TiO_2 can only form CH_4 and CH_3OH with a conduction band potential of -0.5 V vs NHE at $\text{pH}=7$ [46,47]. Similarly, many electrons are required for the production of CH_4 (8 electrons), CH_3OH (6 electrons), HCHO (4 electrons) and CO (2 electrons) [48-50].

There are usually two methods which are used for the reduction of CO_2 with H_2O .

Solid liquid interface reaction model: In this case the contact of catalyst with liquid is direct which leads adsorption of water (H_2O) on the surface of catalyst due to limited solubility of CO_2 in H_2O .

Solid vapor interface reaction mode: in this type the contact of catalyst with vapors which causes the formation of H_2 from the reduction of H_2O reduced [51].

When we place TiO_2 or any other doped catalysts on a catalysts holder which is encircled by CO_2 and water vapors then production of CH_4 increased three times as compared to catalysts dispersed in water (H_2O).

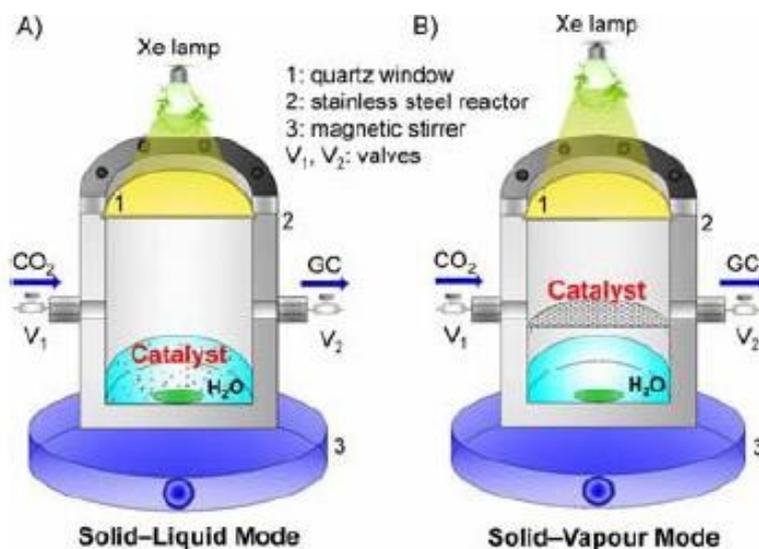


Figure 2. Two characteristic reaction representations for photocatalytic reduction of CO_2 in the presence of H_2O .

TiO_2 Photocatalysts Modified by Doping

The spectral response of TiO_2 can be increased through narrowing electronic properties by doping and or deposition and by altering optical responses. Interfacial charge transfer process can be improved by depositing metal ions on TiO_2 surface for the photo-induced charge carriers which act as a sink. There are many metallic dopants which are used for TiO_2 which are listed here noble metals such as (Pt, Au, Pd, Rh, Ni, Cu, Sn, Ag), rare-earth metals such as (La, Ce, Pr, Nd, Sm, Eu, Dy, Gd), transition metals such as (Zn, Fe, Mn, Co, Pd, Ni), etc. many other metals and non-metal ions [52].

Doping with metals

TiO_2 doped with metals to reduce band gap energy or increase wavelength seems to be a promising method. Due to doping materials an energy level filled with electrons can either add in the band- gap. These electrons can excite into conduction band (N-type) and leaves a mobile hole in the valence band (p-type) or electron hole pairs are created due to irradiation of visible light [53]. In **Figures 2 and 3**, Doping of TiO_2 Nano photocatalysts worked by many researchers.

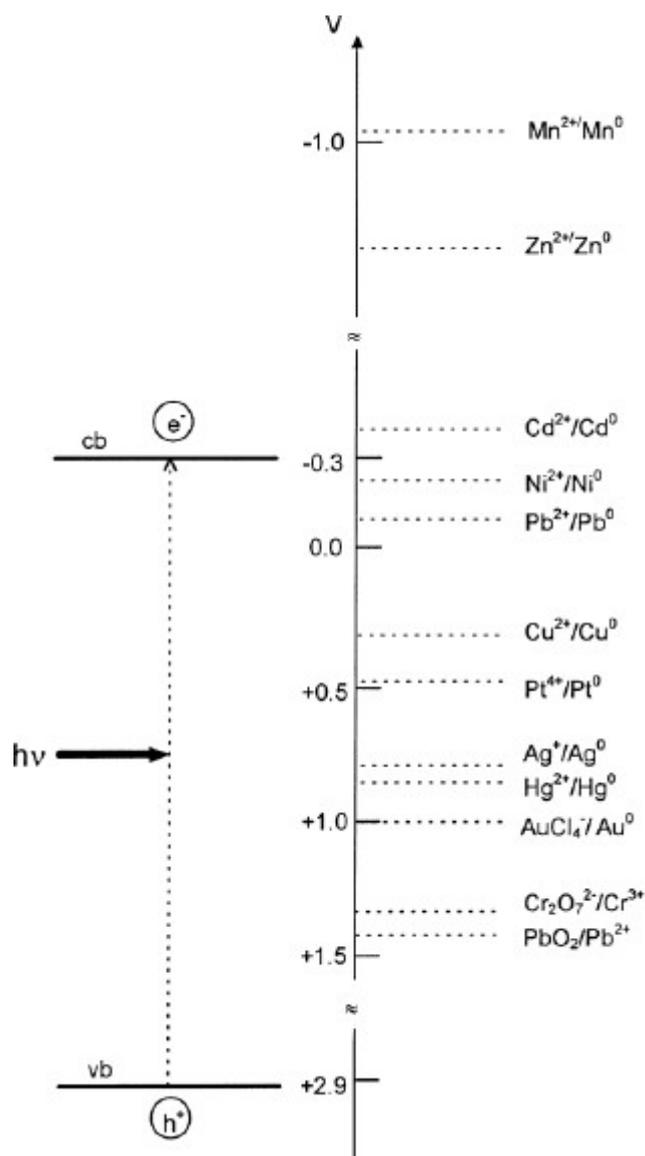


Figure 3. Redox potential positions of many coupled metals show the valence and conduction band energies of TiO_2 Degussa P-25 [54].

Perdew et al. [55] modified TiO_2 and other semiconductors to enhance photocatalytic activity using Density Functional Theory (DFT) calculations by the existence of silver (Ag) and platinum (Pt) octamer clusters. By the existence of Ag and Pt, how we show the CO_2 adsorption on the surface of TiO_2 anatase. The Perdew–Burke–Ernzerhof (PBE) functional of the generalized gradient approximation (GGA) [56] using the VASP (Vienna Ab Initio Simulation package) code [57,58] was used to perform the DFT calculations. The presence of Ag and Pt octamer clusters modified CO_2 adsorption on the surface of anatase TiO_2 using DFT calculations where no bonding between CO_2 and octamer denotes the electron density on the surface of TiO_2 by modification of TiO_2 properties. In short Ag and Pt doping which is used for the increase of photocatalytic activity of TiO_2 .

Smirnova et al. [59] synthesized mesoporous nanosize Titania films doped with metal ions such as Co^{2+} , Ni^{2+} , Mn^{3+} , and Cu^{2+} ions electrodes (Mesoporous TiO_2 , $\text{Co}^{n+}/\text{TiO}_2$, $\text{Ni}^{n+}/\text{TiO}_2$, $\text{Mn}^{n+}/\text{TiO}_2$, and $\text{Cu}^{n+}/\text{TiO}_2$ films and powders) [60] by using sol-gel technique and characterization of the prepared samples by optical spectroscopy, XRD and Brunauer Emmett and Teller. Photoelectron chemical measurements which are used to estimate the bandgap energy and location of smooth band potentials. Transition metal doped film shows high photo current quantum product as well as photo and electrochemical activity. Undoped samples Mn^+/TiO_2 (M-Co, Ni, Cu) electrodes which have less dopant contents shows maximum efficiency of dissolved oxygen in electro catalytic reduction. One current wave which is present in Polarization curves of TiO_2 , $\text{TiO}_2/\text{Ni}^{2+}$, $\text{TiO}_2/\text{Co}^{2+/3+}$, and $\text{TiO}_2/\text{Mn}^{3+}$ electrodes. This shows reaction move ahead without the production of H_2O_2 . Finally, the Nano porous structure of Mn^+/TiO_2 film which have average size of 2.5-6 nm and specific surface area 147 to 224 m^2/g (pure TiO_2).

Gregor et al. [61] synthesized $\text{TiO}_2\text{-WO}_3$ composites with two unlike types of TiO_2 morphologies (R- $\text{TiO}_2\text{-WO}_3$) nanorods and (P- $\text{TiO}_2\text{-WO}_3$) polyhedral nanoparticles by using impregnation method. These composites finally used to study the electron trapping (ET) energy states effect of $\text{TiO}_2\text{-WO}_3$ composites and their effect on photocatalytically degradation of bisphenol A. Alkaline hydrothermal method used to prepare TiO_2 nanorods by commercially available high surface area TiO_2 . WO_3 is intermixed on the TiO_2 surface of nanorods. TEM analysis of R- $\text{TiO}_2\text{-WO}_3$ showed that by enhancing the concentration of WO_3 the crystal structure of TiO_2 was changed. Multiphase systems with WO_3 dispersed onto anatase TiO_2 was observed in case of P- $\text{TiO}_2\text{-WO}_3$ composite. Moreover, 'the P- $\text{TiO}_2\text{-WO}_3$ composite which have strong surface acidic sites than R- $\text{TiO}_2\text{-WO}_3$ composites. The acidic sites were absent on R- $\text{TiO}_2\text{-WO}_3$ composites'. To study the depth of electron trapping this information is suitable. Infrared spectroscopy measurements used to study the Ultra violet light irradiation, electron hole-pair excitation, deterioration of both $\text{TiO}_2\text{-WO}_3$ and knowledge about conduction band and surface trapping (ST) states of nanocomposites. Nanoparticles which have ellipsoid shape showed the image of TEM P-500 sample which have 30 nm length and 20 nm diameter R-500 and P+4.40 solids which have narrow trapping sites showed by time resolved FTIR. Fast hole recombination which are present in P-500 and R+4.40 samples. Finally, photocatalytic activity improved by adding WO_3 in P-500 based materials and in R-500 depreciates, photocatalytic BPA degradation experiments used for confirmation.

Sandeep et al. [62] prepared Cu-doped TiO_2 anatase nanorods by a hydrothermal method. By annealing the hydrothermally synthesized Cu-doped TiO_2 nanotubes at 500°C temperature in different atmosphere such as argon and air. Cu-doped TiO_2 anatase nanorods were obtained with average length 100 nm and a mean diameter of 15-25 nm as confirmed by TEM. XRD showed the intrinsic ferromagnetic nature of prepared sample. Ferromagnetic nature of prepared sample is due to defects revealed by photoluminescence (PL) spectrum. This ferromagnetic nature of Cu-doped TiO_2 found maximum in argon than air. The oxygen vacancies were quenched due to annealing and ferromagnetic order was found minimum. So, there is a close inter-relationship with behavior of oxygen vacancies due to minimum ferromagnetic order.

Co-doping modification

Mengqiu et al. [63] used a facile hydrothermal method which prepared the novel $\text{TiO}_2\text{-ZrO}_2$ -coated gold (Au) Nano catalyst ($\text{ZrO}_2\text{-TiO}_2\text{/Au}$). For the characterization of prepared composites following techniques used such as, TEM, EDX, FTIR, XRD, UV-vis and XPS analyses to show the arrangement, construction, and morphology of $\text{ZrO}_2\text{-TiO}_2$ hollow spheres. The gold Nano particles size was estimated to be 3-5 nm in diameter range which worked as a catalyst in the reduction of 4-nitrophenol to 4-aminophenol by NaBH_4 . Due to mixed oxide synergistic effect $\text{TiO}_2\text{/Au}$ and $\text{ZrO}_2\text{/Au}$, $\text{ZrO}_2\text{-TiO}_2\text{/Au}$ NPs showed highest photo activity. Finally, sample (ZT/Au NPs) calcined at 550, 300 and room temperature, respectively to gain the required sample. The highest thermal stability and reactivity which the sample got at 550.

Zhou et al. [64] first of all prepared the TiO_2 nanocrystals by solvothermal method with the use of co-exposed [1] and facets [65]. Then Pt and Cu_2O co-deposited by chemical reduction method on TiO_2 nanocrystals with the use of NaBH_4 . Then we studied the photocatalytic performance of TiO_2 where Pt increased the productivity of CH_4 and H_2 than Cu_2O . Finally, due to co-deposition of Pt and Cu_2O on TiO_2 nanocrystals the amount of H_2 production decreased but CO_2 converted into CH_4 . From characterization Pt generated photo generated electrons and also increase the electron density on the catalyst, which were beneficial for the formation of CH_4 [66]. Due to deposition of metal species the XRD pattern showed that crystal structure of anatase TiO_2 did not affected. Due to loading of metal species the surface areas, pore size, and pore structure of TiO_2 nanocrystals affected. TiO_2 nanocrystals which have side length and thickness approximately 50 nm and 20 nm [7].

Ruirui et al. [67] prepared a heterojunction composites ($\text{g-C}_3\text{N}_4\text{/TiO}_2$) with maximum surface area by hydrothermal procedure followed by calcination with use of titanium tetrachloride (TiCl_4) and melamine act as a precursor. This semiconductor photocatalysts heterojunction composites prepared to make it active for visible light for the degradation of environmental contaminants. Where HCl acted as a proton source to acidify the melamine. This heterojunction composites showed high photocatalytic performance so due to high photocatalytic activity it has high specific (ultrahigh) external area for environmental and energy applications. Across the (002) and (100) planes (JCPDS No.87-1526), the main diffraction peaks were found at 27.7 and 13.2. According to the Scherrer equation the crystallite size of anatase phase was valued by lengthening of (101) peak.

Hamed et al. [68] synthesized first of all TiO_2 nanowires by alkaline hydrothermal process then by a mixture of hydrothermal and photo deposition techniques two novel photocatalysts were prepared such as Gr/Pd/ TiO_2 -NPs and Gr/Pd/ TiO_2 -NWs. Finally, the prepared sample were categorized by XRD, FT-IR, SEM, DRS, TEM, ICP-OES, EDS and TGA analysis. From feedbacks it was showed that the prepared composites (Gr/Pd/ TiO_2 -NWs and Gr/Pd/ TiO_2 -NPs) have highest photocatalytic activity due to high obtainable surface area of TiO_2 with excessive potential for recycling and stability over five departure cycles.

Asghar et al. [69] synthesized the ternary nanocomposites (PbSe-Gr-TiO_2) using ultra sonication method by loading 6% GO for more efficient photocatalytic activity after the required time for reaction 48 hour. The photocatalytic activity of the

prepared ternary nanocomposites was tested by reduction of CO₂ into useful hydrocarbons such as CH₄, CH₃OH etc. Finally, we characterized the prepared nanocomposites by XRD, SEM, Raman, HRTEM and DRS techniques. This all work which has done to improve the output of graphene-based TiO₂ photocatalysts.

Non-metal doping modification

Jian et al. [70] synthesized C-doped TiO₂ (C-TiO₂) single crystal nanorods by facile hydrothermal method using CPS /TiO₂ as an antecedents of carbon source and TiO₂ nanorods to improve contact probability and formation possibility of C-TiO₂ single crystal. Cationic polystyrene spheres (CPS) prepared by hydrothermal reaction then we have done pyrolysis in a N₂ atmosphere at 450 of CPS to made final product. Finally, the prepared sample (C-TiO₂) were characterized by SEM, TEM, STEM Mapping, UV-vis spectroscopy, XRD, and XPS. As a result, C-TiO₂ nanorods which became active for visible light irradiation then it showed the photocatalytic efficiency of visible light for the degradation of many organic pollutants such as methylene blue, Rhodamine B and p- nitro phenol.

Chang-gen et al. [71] synthesized the H₃PW₁₂O₄₀/TiO₂ nanometer photocatalysts by one step hydrothermal method or modification of TiO₂ with phosphor tungstic acid (H₃PW₁₂O₄₀). The prepared sample was characterized by FTIR spectroscopy, XRD, Nitrogen adsorption and desorption method and SEM. The diameter and specific surface area of the prepared catalyst are 3.8 nm and 177.9 m²/g. Finally, we found that the H₃PW₁₂O₄₀/TiO₂ photocatalysts prepared by hydrothermal method was very suitable and have high photocatalytic activity. To check the photocatalytic activity, we utilized the H₃PW₁₂O₄₀/TiO₂ to sterilize the methyl orange. Some researchers were improving the efficiency of catalyst by loading H₃PW₁₂O₄₀ on the surface of TiO₂ using impregnation method [72].

FUTURE PERSPECTIVES AND SUMMARY

In this type of review, systematically recent progress for the modification of TiO₂ has been done to reduce the CO₂ into useful fuel by using photocatalytical reactor. For chemical and material science the modification of TiO₂ is growing day by day towards success. TiO₂ has been modified by many techniques which leads this modified TiO₂ active for visible sun light for the reduction of carbon dioxide (CO₂) into fuel. Due to modification of TiO₂ several advantages and disadvantages occurs. Critical investigation for the reduction of CO₂ focus overall the efficiency of desired photocatalytic reaction. Detailed study about TiO₂ required full attention. For wide practical applications of modified TiO₂ recycling is much crucial. In order to achieve high level of efficiency the TiO₂ modification is necessary. The efficient role is played by the redox potential and electron density of surface of TiO₂ to find out the final product of proteolytically CO₂ reduction towards useful hydrocarbons.

In summarized form, except previous illustration the modification of TiO₂ has not been fully explained for the conversion of CO₂ into useful product but it should be more helpful for the development of technology in future. Furthermore, the modified TiO₂ will be much helpful to achieve maximum feedback by converting CO₂ into useful product.

ACKNOWLEDGMENTS

This research was supported by University of Gujrat, Hafiz Hayat, main Campus. The authors are much grateful for support during completion of research work.

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