

# Critical Review on Modification of TiO<sub>2</sub> for the Reduction of CO<sub>2</sub>

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## Review Article

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## ABSTRACT

With the passage of time the consumption of fossil fuels is increasing which causes to eliminate more and more greenhouse gases such CO<sub>2</sub> in our atmosphere. CO<sub>2</sub> is much harmful for us causes energy Crises etc. One of the best solution to reduce the quantity of CO<sub>2</sub> into valuable sources such as CH<sub>4</sub>, HCO<sub>2</sub>H, CH<sub>2</sub>O, and CH<sub>3</sub>OH by preparing metal oxide semiconducting materials with the use of metal doping and coupling with other metal oxides. Metal oxide (TiO<sub>2</sub>) has been used for the photo catalytically reduction of CO<sub>2</sub> due its non-toxicity, cheapness and environmentally friendly. Modification of TiO<sub>2</sub> has concerned many interests due to maximum light absorption, decrease recombination rate, increase surface area to volume ratio, increase CO<sub>2</sub> adsorption ability and enhanced activity of TiO<sub>2</sub> for the conversion of CO<sub>2</sub> into valuable sources. In this review paper, recent work on TiO<sub>2</sub> 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<sup>[1,2]</sup>. Emission of CO<sub>2</sub> is increasing in planet which causes to enhance global warming<sup>[3]</sup>. Our problem of environmental energy crises is solved by the conversion of CO<sub>2</sub> into useful fuel by using TiO<sub>2</sub> nanocomposites. In 1972 First of all Honda and Fujishima discovered photoelectrochemical water splitting by using TiO<sub>2</sub> semiconducting electrodes which was found helpful to meet future energy crisis problems<sup>[4]</sup>. Except water splitting into hydrogen and oxygen, photovoltaically conversion of CO<sub>2</sub> into valuable fuel by using metal oxide (TiO<sub>2</sub>) semiconducting photocatalysts as a primary requirement which also deal with our environmental energy crisis issues<sup>[5-9]</sup>.

Photo catalytically conversion of CO<sub>2</sub> into solar fuels such as methane, methanol (CH<sub>3</sub>OH), HCO<sub>2</sub>H, CH<sub>2</sub>O, etc. and water splitting (H<sub>2</sub>O) into hydrogen and oxygen have been extensively studied<sup>[10]</sup>. Photo catalytical reactor is the best way which is used for the conversion of CO<sub>2</sub> into valuable fuels. There are many metal oxide materials which have been used as photocatalysts under ultraviolet visible irradiations such as ZnO, ZrO<sub>2</sub>, Ga<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, MgO, CaO, and Al<sub>2</sub>O<sub>3</sub><sup>[11-14]</sup>. Furthermore, photocatalytic reduction of CO<sub>2</sub> which also have been done by metal sulfides such as ZnS<sup>[15-17]</sup> CdS<sup>[10,15,18]</sup> and Bi<sub>2</sub>S<sub>3</sub><sup>[19]</sup>. In addition, other polyoxometalates (CaFe<sub>2</sub>O<sub>4</sub>) and semiconductors such as GaP or SiC which have also been utilized as a photocatalysts for the reduction of CO<sub>2</sub> in our environment under UV Visible irradiations<sup>[20,21]</sup>. 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<sup>[22]</sup> and charge separation is inefficient due to recombination of charge carriers<sup>[23-26]</sup>. Anatase TiO<sub>2</sub> has been proved extremely good semiconducting photocatalyst for the conversion of CO<sub>2</sub>

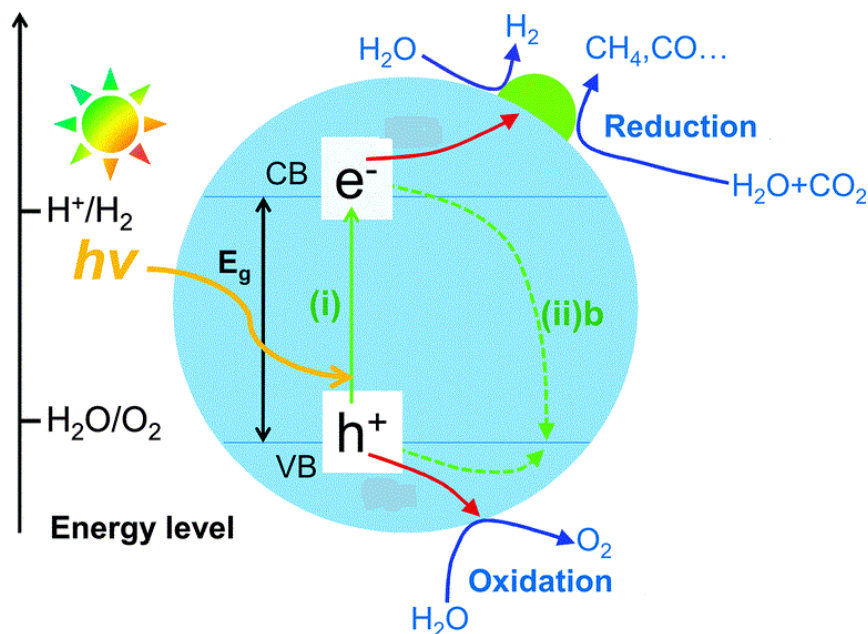
into useful hydrocarbons due to its properties such as non-toxicity, chemical stability and photocatalytic activity [27]. Though, TiO<sub>2</sub> semiconducting material is not actively available for visible light irradiation due to large bandgap (3.0~3.2 eV) and approximately only 5% solar light is utilized for the photocatalytic reaction on the surface of TiO<sub>2</sub> [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 TiO<sub>2</sub> 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<sup>-</sup>/h<sup>+</sup>) 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 (H<sub>2</sub>O) splitting using electrodeposition method a p-type semiconductor Zinc telluride (ZnTe) has been deposited on TiO<sub>2</sub> 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 TiO<sub>2</sub> such as impurity doping, metal deposition, Alkali modification, Heterojunction construction and carbon based material loadings for the photocatalytic reduction of CO<sub>2</sub> 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 TiO<sub>2</sub> for more efficient efficiency of CO<sub>2</sub> reduction. Finally, conclusion and future outlook of surface modified TiO<sub>2</sub> semiconductor photocatalysts are examined.

## MECHANISM PHOTOCATALYTICALLY FOR CO<sub>2</sub> REDUCTION

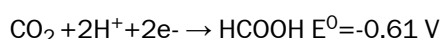
There are main three steps used for the reduction of CO<sub>2</sub> into valuable hydrocarbons with water (H<sub>2</sub>O) as shown in Figures 1-3. Firstly, when we irradiate appropriate light with energy equal or greater than the band gap energy of semiconductor then generation of electron hole pairs 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<sup>-</sup>/h<sup>+</sup> pairs together the emission of energy in the form of heat take place. Thirdly, the reduction of CO<sub>2</sub> causes due to photogenerated electrons by the adsorption on catalyst surface into CO, HCOOH, CH<sub>3</sub>OH or CH<sub>4</sub>. Where oxidation of H<sub>2</sub>O into O<sub>2</sub> due to holes occurs. In splitting of H<sub>2</sub>O into O<sub>2</sub> the first and second steps plays the same role. The recombination of charge is much faster (~10<sup>-9</sup> s) process as compared to the process of reaction (~10<sup>-3</sup>-10<sup>-8</sup> s).

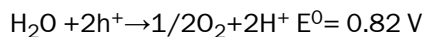
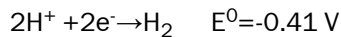
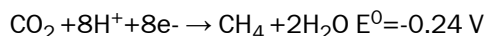
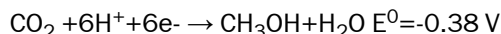
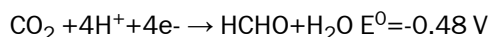
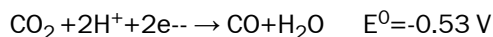


**Figure 1.** Schematically Basic mechanism of photo catalytically reduction of CO<sub>2</sub> with H<sub>2</sub>O on a semiconductor photocatalysts (TiO<sub>2</sub>).

Several possible redox potentials and reactions related to reduction of CO<sub>2</sub> summarized below in which useful hydrocarbons such as CO, CH<sub>4</sub>, CH<sub>3</sub>OH, HCOOH and HCHO are all required products.

[E<sup>0</sup> (V) vs. NHE (pH=7)]





During photo catalytically  $\text{CO}_2$  reduction reaction  $\text{TiO}_2$  can only form  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$  with a conduction band potential of  $-0.5 \text{ V}$  vs NHE at  $\text{pH}=7$  [46,47]. Similarly, many electrons are required for the production of  $\text{CH}_4$  (8 electrons),  $\text{CH}_3\text{OH}$  (6 electrons),  $\text{HCHO}$  (4 electrons) and  $\text{CO}$  (2 electrons) [48-50].

There are usually two methods which are used for the reduction of  $\text{CO}_2$  with  $\text{H}_2\text{O}$ .

**Solid liquid interface reaction model:** In this case the contact of catalyst with liquid is direct which leads adsorption of water ( $\text{H}_2\text{O}$ ) on the surface of catalyst due to limited solubility of  $\text{CO}_2$  in  $\text{H}_2\text{O}$ .

**Solid vapor interface reaction mode:** in this type the contact of catalyst with vapors which causes the formation of  $\text{H}_2$  from the reduction of  $\text{H}_2\text{O}$  reduced [51].

When we place  $\text{TiO}_2$  or any other doped catalysts on a catalysts holder which is encircled by  $\text{CO}_2$  and water vapors then production of  $\text{CH}_4$  increased three times as compared to catalysts dispersed in water ( $\text{H}_2\text{O}$ ).

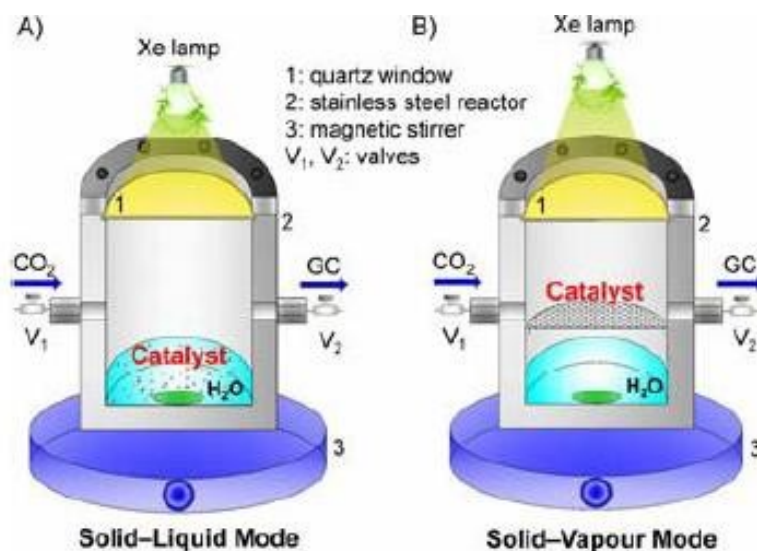


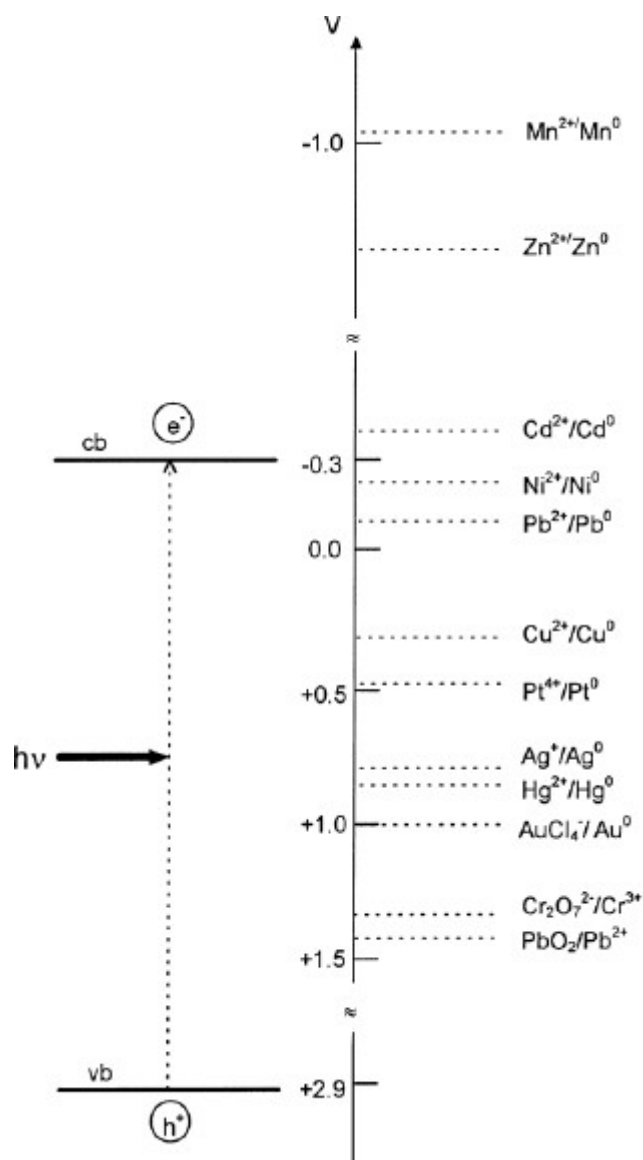
Figure 2. Two characteristic reaction representations for photocatalytic reduction of  $\text{CO}_2$  in the presence of  $\text{H}_2\text{O}$ .

### **$\text{TiO}_2$ Photocatalysts Modified by Doping**

The spectral response of  $\text{TiO}_2$  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  $\text{TiO}_2$  surface for the photo-induced charge carriers which act as a sink. There are many metallic dopants which are used for  $\text{TiO}_2$  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*

$\text{TiO}_2$  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  $\text{TiO}_2$  Nano photocatalysts worked by many researchers.



**Figure 3.** Redox potential positions of many coupled metals show the valence and conduction band energies of  $\text{TiO}_2$  Degussa P-25 [54].

Perdew et al. [55] modified  $\text{TiO}_2$  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  $\text{CO}_2$  adsorption on the surface of  $\text{TiO}_2$  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  $\text{CO}_2$  adsorption on the surface of anatase  $\text{TiO}_2$  using DFT calculations where no bonding between  $\text{CO}_2$  and octamer denotes the electron density on the surface of  $\text{TiO}_2$  by modification of  $\text{TiO}_2$  properties. In short Ag and Pt doping which is used for the increase of photocatalytic activity of  $\text{TiO}_2$ .

Smirnova et al. [59] synthesized mesoporous nanosize Titania films doped with metal ions such as  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{3+}$ , and  $\text{Cu}^{2+}$  ions electrodes (Mesoporous  $\text{TiO}_2$ ,  $\text{Co}^{n+}/\text{TiO}_2$ ,  $\text{Ni}^{n+}/\text{TiO}_2$ ,  $\text{Mn}^{n+}/\text{TiO}_2$ , 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  $\text{Mn}^+/\text{TiO}_2$  (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  $\text{TiO}_2$ ,  $\text{TiO}_2/\text{Ni}^{2+}$ ,  $\text{TiO}_2/\text{Co}^{2+/3+}$ , and  $\text{TiO}_2/\text{Mn}^{3+}$  electrodes. This shows reaction move ahead without the production of  $\text{H}_2\text{O}_2$ . Finally, the Nano porous structure of  $\text{Mn}^+/\text{TiO}_2$  film which have average size of 2.5-6 nm and specific surface area 147 to 224  $\text{m}^2/\text{g}$  (pure  $\text{TiO}_2$ ).

Gregor et al. [61] synthesized  $\text{TiO}_2\text{-WO}_3$  composites with two unlike types of  $\text{TiO}_2$  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  $\text{TiO}_2$  nanorods by commercially available high surface area  $\text{TiO}_2$ .  $\text{WO}_3$  is intermixed on the  $\text{TiO}_2$  surface of nanorods. TEM analysis of R- $\text{TiO}_2\text{-WO}_3$  showed that by enhancing the concentration of  $\text{WO}_3$  the crystal structure of  $\text{TiO}_2$  was changed. Multiphase systems with  $\text{WO}_3$  dispersed onto anatase  $\text{TiO}_2$  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  $\text{WO}_3$  in P-500 based materials and in R-500 depreciates, photocatalytic BPA degradation experiments used for confirmation.

Sandeep et al. [62] prepared Cu-doped  $\text{TiO}_2$  anatase nanorods by a hydrothermal method. By annealing the hydrothermally synthesized Cu-doped  $\text{TiO}_2$  nanotubes at  $500^\circ\text{C}$  temperature in different atmosphere such as argon and air. Cu-doped  $\text{TiO}_2$  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  $\text{TiO}_2$  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  $\text{NaBH}_4$ . 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  $\text{TiO}_2$  nanocrystals by solvothermal method with the use of co-exposed [1] and facets [65]. Then Pt and  $\text{Cu}_2\text{O}$  co-deposited by chemical reduction method on  $\text{TiO}_2$  nanocrystals with the use of  $\text{NaBH}_4$ . Then we studied the photocatalytic performance of  $\text{TiO}_2$  where Pt increased the productivity of  $\text{CH}_4$  and  $\text{H}_2$  than  $\text{Cu}_2\text{O}$ . Finally, due to co-deposition of Pt and  $\text{Cu}_2\text{O}$  on  $\text{TiO}_2$  nanocrystals the amount of  $\text{H}_2$  production decreased but  $\text{CO}_2$  converted into  $\text{CH}_4$ . From characterization Pt generated photo generated electrons and also increase the electron density on the catalyst, which were beneficial for the formation of  $\text{CH}_4$  [66]. Due to deposition of metal species the XRD pattern showed that crystal structure of anatase  $\text{TiO}_2$  did not affected. Due to loading of metal species the surface areas, pore size, and pore structure of  $\text{TiO}_2$  nanocrystals affected.  $\text{TiO}_2$  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 ( $\text{TiCl}_4$ ) 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  $\text{TiO}_2$  nanowires by alkaline hydrothermal process then by a mixture of hydrothermal and photo deposition techniques two novel photocatalysts were prepared such as Gr/Pd/ $\text{TiO}_2$ -NPs and Gr/Pd/ $\text{TiO}_2$ -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/ $\text{TiO}_2$ -NWs and Gr/Pd/ $\text{TiO}_2$ -NPs) have highest photocatalytic activity due to high obtainable surface area of  $\text{TiO}_2$  with excessive potential for recycling and stability over five departure cycles.

Asghar et al. [69] synthesized the ternary nanocomposites ( $\text{PbSe-Gr-TiO}_2$ ) 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 CO<sub>2</sub> into useful hydrocarbons such as CH<sub>4</sub>, CH<sub>3</sub>OH 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 TiO<sub>2</sub> photocatalysts.

#### *Non-metal doping modification*

Jian et al. [70] synthesized C-doped TiO<sub>2</sub> (C-TiO<sub>2</sub>) single crystal nanorods by facile hydrothermal method using CPS /TiO<sub>2</sub> as an antecedents of carbon source and TiO<sub>2</sub> nanorods to improve contact probability and formation possibility of C-TiO<sub>2</sub> single crystal. Cationic polystyrene spheres (CPS) prepared by hydrothermal reaction then we have done pyrolysis in a N<sub>2</sub> atmosphere at 450 of CPS to made final product. Finally, the prepared sample (C-TiO<sub>2</sub>) were characterized by SEM, TEM, STEM Mapping, UV-vis spectroscopy, XRD, and XPS. As a result, C-TiO<sub>2</sub> 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 H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/TiO<sub>2</sub> nanometer photocatalysts by one step hydrothermal method or modification of TiO<sub>2</sub> with phosphor tungstic acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>). 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 m<sup>2</sup>/g. Finally, we found that the H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/TiO<sub>2</sub> photocatalysts prepared by hydrothermal method was very suitable and have high photocatalytic activity. To check the photocatalytic activity, we utilized the H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/TiO<sub>2</sub> to sterilize the methyl orange. Some researchers were improving the efficiency of catalyst by loading H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> on the surface of TiO<sub>2</sub> using impregnation method [72].

## FUTURE PERSPECTIVES AND SUMMARY

In this type of review, systematically recent progress for the modification of TiO<sub>2</sub> has been done to reduce the CO<sub>2</sub> into useful fuel by using photocatalytical reactor. For chemical and material science the modification of TiO<sub>2</sub> is growing day by day towards success. TiO<sub>2</sub> has been modified by many techniques which leads this modified TiO<sub>2</sub> active for visible sun light for the reduction of carbon dioxide (CO<sub>2</sub>) into fuel. Due to modification of TiO<sub>2</sub> several advantages and disadvantages occurs. Critical investigation for the reduction of CO<sub>2</sub> focus overall the efficiency of desired photocatalytic reaction. Detailed study about TiO<sub>2</sub> required full attention. For wide practical applications of modified TiO<sub>2</sub> recycling is much crucial. In order to achieve high level of efficiency the TiO<sub>2</sub> modification is necessary. The efficient role is played by the redox potential and electron density of surface of TiO<sub>2</sub> to find out the final product of proteolytically CO<sub>2</sub> reduction towards useful hydrocarbons.

In summarized form, except previous illustration the modification of TiO<sub>2</sub> has not been fully explained for the conversion of CO<sub>2</sub> into useful product but it should be more helpful for the development of technology in future. Furthermore, the modified TiO<sub>2</sub> will be much helpful to achieve maximum feedback by converting CO<sub>2</sub> into useful product.

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