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Review

Epigrammatic status and perspective of sequestration of carbon dioxide: Role of TiO_2 as photocatalyst

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A B S T R A C T

Owing to tremendous increasing Carbon dioxide emissions, the environment and our lives have been affected by global warming and climate changes. There is a growing need to mitigate CO_2 emissions. Some of the strategies to mitigate CO_2 emissions are energy conservation, carbon capture and storage and using CO_2 as a raw material in chemical processes. One of the best routes to remedy CO_2 is to transform it to hydrocarbons via photo reduction. The paper presents the trends on the different methods of conversion of carbon dioxide into hydrocarbons. Among various methods, use of photo catalyst TiO_2 is widely studied due to its comparatively low cost, low toxicity and its ability to resist photo corrosion. The importance of titania correlating with its properties is presented. Different doping of TiO_2 is mentioned. The review concluded that TiO_2 represents an effective photo catalyst for conversion of carbon dioxide leading to purification of environment and solution to energy crisis.

1. Introduction

With the advent of industrialization to meet the demands of ever growing population globally, the expenditure on meetings energy is explosively increasing. World energy consumption doubled between 1970 and 2000. It is expected to double again between now and 2050. The use of energy is still uneven, with electricity consumption of 83 kW-h in the least developed countries as against with an average of 8053 kWh in OECD countries (Organisation for Economic Cooperation and Development).

Due to inherent higher energy density, abundance, and the economic dependence of modern society on the acquisition and trade of fossil fuels we are primarily dependent on them as source of energy. They will continue their top rank as power generator and industry built up in future as well. In the current period, over 85% of this energy demand is being supplied by flaming of fossil fuels (Rackley, 2010). The byproduct of the process of burning of fossil fuels mainly comprises of carbon dioxide, which is directly released into the atmosphere, leading to disturbance in carbon balance of our planet. The carbon balance of earth is steady over hundreds of millions of years. Since the commencement of industrial era, around 1750, the CO_2 concentration in atmosphere has increased from 280 to 407 ppm as per mid of 2017 (ESRL, 2017).

Carbon dioxide is naturally present in the atmosphere as part of the Earth's carbon cycle (the natural circulation of carbon among the atmosphere, oceans, soil, plants, and animals). Human activities are altering the carbon cycle–both by adding more CO_2 to the atmosphere and by adversely influencing the ability of natural sinks, like forests, oceans and weathering processes, to remove CO_2 from the atmosphere. The main human activity that emits CO_2 is the combustion of fossil fuels (coal, natural gas, and oil) for energy and transportation, although certain industrial processes and land-use changes also emit CO_2.

Thus, CO_2 has often been cited as the primary anthropogenic greenhouse gas (GHG) as well as the foremost culprit in climate change. Potential and effective methods are urgently required to minimize the climate change by controlling or reducing CO_2 emissions in environment and this is needed to study all potential methods for their effectiveness. In the interim period to a low-carbon society, however, it is imperative to reduce anthropogenic CO_2 emission (Roosa and Jhaveri, 2009). In their independent work Xu and Moulijn (1996), Yang et al. (2008) and Mikkelsen et al. (2010) reported three principles of reduce, reuse and recycle CO_2 namely, CO_2 capture, CO_2 cache (store), and CO_2 convert (or the three Cs). The first strategy requires energy efficient improvements and search for sustainable, economically viable energy sources in spite of using fossil fuels. Storage of CO_2 involving the development of new technologies for capture and seizure of CO_2, is a relatively well established process (Yang et al., 2008; Hunt et al., 2010; Ferey et al., 2011). Yet, constant research is on to improve their efficiency and efficacy (Wen et al., 2013). The conversion of CO_2 into fuels is a significant solution for the environmental issues like global warming and conservation of current fossil fuels. Over the last years, many studies have been done on sequestration of carbon dioxide. In this

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regard different approaches include biomass production, thermochemical, electrochemical and photocatalytic conversion. In photocatalytic conversion nanotechnology has its own merits over the other traditional approaches in effective conversion of CO_2. The purpose of present study is to highlight the different approaches for conversion of CO_2 and the advantage of use of nanoparticle of titania for the sequestration.

Conversion of CO_2

It is an economical, safe and renewable carbon source which can decrease its contribution in alleviating global climate changes by its conversion into hydrocarbons which also gives us opportunity for exploration of wide methods for catalytic and industrial development in this field. Since early 1900s the conversion of carbon dioxide into useable hydrocarbons is in process. The Sabatier and the Fischer-Tropsch processes are the methods that involve the conversion of hydrogen and carbon dioxides into hydrocarbons, especially for hydrocarbons used for fuels. The Sabatier process involves the conversion of CO_2 and hydrogen gas into methane and water in the presence of nickel catalyst at high temperatures and high pressures (Sabatier, 2005). The process has been considered in the research of alternative fuels.

Sabatier Reaction

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

Franz Fischer and Hans Tropsch invented the Fischer-Tropsch process in the 1920s (Transportation and Programs Division, 2002). The process involves two steps and is also seen as an alternative fuel source. The first step is the partial oxidation of coal or natural gas fuels into hydrogen gas and carbon oxide. The carbon oxide and hydrogen are then converted into more useful methanol and methane fuels. Although it is still currently being used, the Fischer-Tropsch process was a major factor in the German effort in World War II, because they did not have an abundance of oil, but did have vast amounts of coal to produce synthetic oil. But the process involves use of non-renewable source of energy for obtaining carbon dioxide.Fig. 1.

Fischer-Tropsch Process

$$CH_4 + 1/2O_2 \rightarrow 2H_2 + CO$$

$$(2\,n+1)H_2 + nCO \rightarrow C_nH_{2n+2}(\text{ex. } CH_4, CH_3OH) + nH_2O$$

Although these methods are still being pursued today, the advancement in conversion of CO_2 into hydrocarbon is mounting day by day as carbon dioxide turns out to be an attractive C1 building block for making organic chemicals, materials and carbohydrates (food). There are many methods for its conversion (Fig. 2).

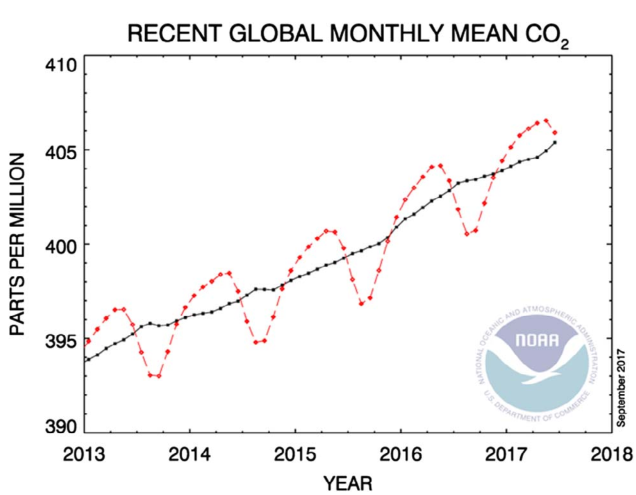

Fig. 1. Atmospheric CO_2 concentration during 2013–2017 showing the continuing and accelerating increase of CO_2 in atmosphere (Dlugokencky, 2016).

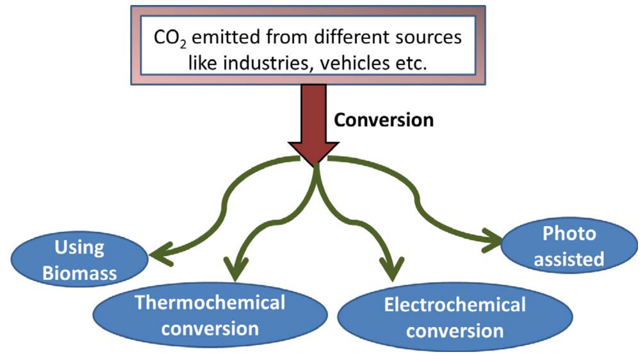

Fig. 2. Methods of conversion of CO_2 into hydrocarbons.

1.1. *Conversion of CO_2 through biomass production*

Bio-Carbon dioxide Conversion and storage (CCS) may be defined as processes in which CO_2 originating from anthropogenic activities is captured and stored. Thus, Biomass fuels utilize the chemical energy fixed by photosynthesis and stored within plants. We can use this chemical energy for creation of heat, used in traditional purposes (such as cooking and space heating) or to produce industrial process heat (viz. paper industry), or it can be converted to electricity or to gaseous or liquid fuels (methane, hydrogen, alcohols, or oils). CCS shows great potential in diminishing the amount of CO_2 released into the atmosphere from combustion processes (Herzog et al., 2000), according to Herzog et al. (2003) it can contribute up to 55% to the mitigation efforts. For instance, recently Oliver et al., demonstrates that carbon dioxide can be converted to 2,3-butandiol by biosynthetic pathway in a model system (Oliver et al., 2013). As depicted in Fig. 3 the general method of conversion of CO_2 can be described, however if CO_2 from biofuel combustion was captured and stored, a net removal of CO_2 from atmosphere would result (Azar et al., 2003).

According to Möllersten et al. (2003), Chisti (2008), the competence of plants to contribute to biofuel production is much lower than that required, thus other suitable alternatives are proposed such as microalgae. In fact, use of microalgae appears the most promising route to biofuel production, as its oil content is markedly higher than other crops. As reported by Chisti (2007), Roy et al. (2010) and reviewed by Roy et al. (2010) the oil content of most algal species have a dry weight oil content more than 30%. In addition, it is well known that the growth of mircroalgae is faster than plants, and it do not require highly fertile land and/ or useful water. Algae can reach solar energy utilization

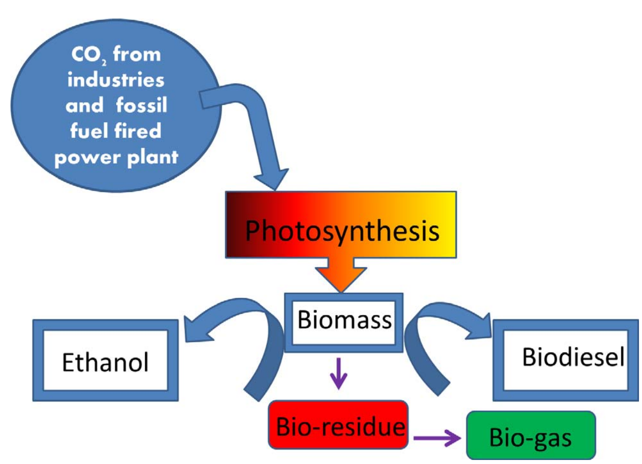

Fig. 3. Pathway of conversion of CO_2 by biomass production.