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Solar fuels vis-à-vis electricity generation from sunlight: The current state-of-the-art (a review)

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Synthesis of solar fuels including methanol from carbon dioxide (CO_2) and water using solar energy or electricity derived from sunlight, which is popularly known as *artificial photosynthesis (AP)*, has been considered to be one of the top-most research priorities all over the world, as on today, as this process can indeed deal with (i) the CO_2 related global warming problem, (ii) synthesis of renewable energy resources, and (iii) storing of energy in the form of liquid fuels with considerably high energy density. By using electricity derived from sunlight, the CO_2 can be reduced into methanol and other value added chemicals using water as a source of protons and electrons in a device called, *artificial leaf*. The development of an efficient AP or *artificial leaves* is possible by the careful analysis and understanding of the complete information available on (i) CO_2 reduction process, (ii) water oxidation or splitting reaction, and (iii) the electricity generation from sunlight. The current state-of-the-art on CO_2 reduction has been thoroughly reviewed in a recent article "Conversion of carbon dioxide into methanol—a potential liquid fuel: fundamental challenges and opportunities", (Renewable and Sustainable Energy Reviews, 31, 2014, 221–257), whereas, the same on (i) water oxidation (or splitting) process, and (ii) the electricity generation from sunlight is yet to be reviewed together from the perspective of creating an efficient and economically viable *artificial leaves*. This article is an attempt to this effect while citing all the up to date relevant references.

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1. Introduction

Synthesis of solar fuels such as, methanol, ethanol, etc., from carbon dioxide (CO_2) and water using sunlight or electricity derived from sunlight is of great importance as these liquid fuels can be directly employed in the present existing energy distribution infrastructure, such as, automobiles without much modifications to their internal combustion (IC) engines, hence, there would not be any severe economical consequences while transforming from fossil fuel energy dependency to non-fossil fuel, renewable or solar energy dependency [1–26]. The conversion of CO_2 into value added chemicals using energy that is not produced from fossil fuels is very important considering today's atmospheric CO_2 related global warming problem as well as the depleting scenario of fossil fuels particularly the oil and coal [27–32]. The concentration of CO_2 in the atmosphere has been raised from 280 ppm in the year 1750 (prior to industrial revolution) to 400 ppm today in the year 2014 [33]. This atmospheric CO_2 raise has been identified to be responsible for most of the noted global warming problem that is not only causing considerable sea level raise all over the world but also the un-usual storms and floods, which are adversely affecting the life, health and economy of the people at several parts of the world [34,35]. Right now, the readily available technology to tackle with this CO_2 related global warming problem is the CO_2 sequestration process, in which the captured CO_2 at major outlets (such as, thermal power plants, etc.), is transported and stored in places such as, un-mineable coal seams, depleted gas and oil reservoirs, and under the deep sea levels [27–34]. This sequestration process is popularly termed as carbon capturing and storing (CCS) process, which is not only expensive, but also has certain issues related to the safety of places, where the captured CO_2 is stored as a part of this process [36]. Of late, it has been found that with the same expenditure incurred for this latter process, instead of disposing off the captured CO_2, it can be converted into several value added chemicals following some of the thermochemical routes, which are at present, practiced in petrochemical industry [37–40]. In this latter case, the value of the products formed could be considered as a bonus when compared with the CCS process. There are also certain other processes such as, stoichiometric, electrochemical, photoelectrochemical, photocatalytic, bio-chemical reactions, etc., in which the captured CO_2 could be converted into a great variety of value added chemicals including methanol and ethanol [14]. The endergonic CO_2 conversion (Fig. 1) could be performed by utilizing different forms of energy as well as protons (or hydrogen) and electrons derived from various sources including water over several catalytic/semiconducting materials and metals [10,12,14]. One of the major bulk chemicals, which is being produced in a stoichiometric reaction, at present, is the polypropylene carbonate that is formed by the copolymerization of CO_2 with propylene oxide. Propylene oxide is a product formed from renewable natural products, oils and fats. Although, CO_2 is also directly employed as (i) a supercritical solvent, (ii) a neutralizing agent, (iii) an inert medium (such as in fire extinguishers), (iv) an inert pressurizing agent, (v) a refrigerant for food preservation, (vi) a beverage carbonating agent, (vii) a gas for creating greenhouse effect, (viii) a laser generating material, and (ix) a component in the synthesis of building materials [41–49], it contributes little to the CO_2 associated global warming mitigation process. If the energy required to perform the reactions (as shown in Fig. 1) is supplied exclusively from the renewable resources including sunlight and electricity derived from the sunlight, it would contribute greatly to the energy storage in the convenient form of fuel chemicals and to the creation of renewable energy resources while mitigating the CO_2 associated global warming problem [21–23,37–40,50,51].

On one hand, the Hubbert's predictions suggest that in the next 40 years, there will be a drastic drop in the recoverable oil resources, and there is a timeframe of only about 20 years from now to find out the alternative energy resources to meet the future energy requirements of the society before the oil resources are completely exhausted [10]. Power plants use fossil fuels (coal, oil or natural gas) to produce electricity. As per today's consumption rate, the available coal reserves will last for another 130 years, natural gas for 60 years, and oil for 42 years [10–12]. Thus, we cannot afford to use these limited and important oil, natural gas and coal resources only to meet just the energy needs instead of several other important products of the future as they are the starting materials for a long list of chemicals and chemical commodities being employed in day-to-day life of the human beings today. Furthermore, these resources are not only for just few decades of the future, but for the continued industrial applications of the next several centuries.

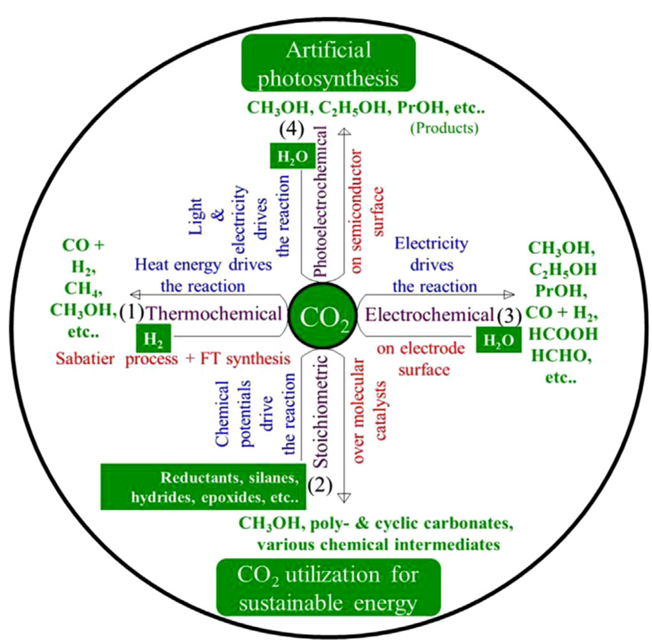

Fig. 1. The major laboratory methods, in which CO_2 can be reduced to value added chemicals using different types of hydrogen and electron sources, and energy vectors.