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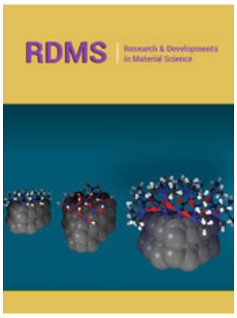

Photocatalyst Filling Multiple Needs: CO_2 Reduction to Extremely Selective Solar Fuels and Oxidative Organic Transformation

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Global warming, ocean acidification and climate change governs around the most produced greenhouse gas CO_2 [1]. The coal-fired power plants are the largest contributors to the uneco-friendly carbon dioxide in the atmosphere. The Industrial Revolution of the 19th century improved the standard of living but was begetting towards the high energy demand that has effectuated in energy crisis at present. The unabated CO_2 in the atmosphere is malignant to the environment. This air of menace has induced various scientist and researchers to build on various methods and techniques for CO_2 reduction or CCUS (Carbon Capture Utilization Sequestration). CCUS focuses on both reduction of CO_2 and its conversion to value added product [2].

Electro-catalytical, thermo-chemical method and use of inorganic and organo-metallic catalyst for reduction are some among the various reduction methods but they come in with few limitations. On the brighter side the electro catalytic reduction of CO_2 to a value enriched product showed high selectivity of the product but its continuous requirement of energy that came from combustion of fossil-fuels for the process marked its darker side [3]. Carbon dioxide being a thermodynamically stable gas (**ΔG^o**≈-394KJ/mol) requires high temperature and pressure for its reduction. The high temperature and pressure requirement in the thermo-chemical reduction process of CO_2 makes the process undesirable [4]. Poor selectivity of product is an inevitable issue of reduction method using inorganic and organo-metallic catalyst [5].

Photo-biocatalysis has pulled a lot of attention due to its utilization of a natural and unbound energy source (solar-light) for reduction of CO_2 to various value-added product such as HCOOH, CH_3OH, CH_4 and many more. The mild working conditions and low input of energy makes the process distinct and advantageous. The integrated system of a photocatalyst with an enzyme (bio-catalyst) serves the basis of CO_2 reduction. In this method the solar energy induces the electrons of a photo-catalyst to reach its active sites from where an electron mediator (Rh complex) aids in converting the NAD^+ cofactor to NADH. The NADH dependent enzyme that has been coupled with the photocatalyst now comes into effect by converting the CO_2 gas into a value-added product with high selectivity. Appropriate band gap, good absorptivity and requisite charge carrier dynamics is pivotal in defining the efficiency of a photocatalyst and ultimately the whole process of reduction of CO_2. The bio-integrated photocatalytic system is a fascinating technique of reduction as it has conventional working conditions, unlimited and natural energy source and high selectivity of the reduced product. The method has been seen to be efficient in converting CO_2 into solar fuels such as HCOOH which can also help in to meet the increasing energy demand of the world to some extent as it shows wide application in DFAFC (Direct Formic Acid Fuel Cell). On this account the bio-integrated photocatalytic system can be considered to fill two needs with one deed [5-7].

Photocatalyst plays an important role in organic transformation into different organic compounds. Photocatalyst in presence of solar radiation leads to solve many chemicals demands in industrial applications. For example, in the field of medicine these organic transformation leads to the formation many chemicals and bioactive molecules which are used as an intermediate in the chemical route of formation of medicines. For example, the organic compound 4-methoxybenzylamines can be transform into 4-methoxy N,N-dimethylbenzylimines via oxidative coupling of the 4-methoxybenzylamines [8] in the presence of photocatalyst which can be used by the pharmaceutical companies as an intermediate for making medicines.

Photocatalysis has also been seen to play a crucial role in the storage of energy i.e NADH regeneration. The NADH or NADPH is the electrons and hydrogen donors in CO_2 reduction method. In industries there are limitations of energy production by the photocatalytic enzyme process because there is a high-cost value of NADH or NADPH also in the photocatalytic process the NADH or the NADPH itself convert into the NAD^+ or $NADP^+$ respectively and they could not regenerate back itself. Therefore, it is necessary to regenerate NADH or NADPH from consumed NAD^+ or $NADP^+$ so that it can be used by the industries in many industrials applications. The regeneration of NADH or NADPH can be done by the using of photocatalyst via artificial photosynthesis. In a reaction medium, containing phosphate buffer solution (NaH_2PO_4-Na_2HPO_4), NAD^+ co-factor, electron mediator (Rh-complex) [9], sacrificial agent (ascorbic acid), light harvesting complex (photocatalyst) were taken. Firstly, in dark medium for 30mins and then further in light medium for 120mins. Therefore, in light medium there is high increase of NADH or NADPH (calculated by reported UV spectrometry) whereas, in dark medium there was no any formation of NADH or NADPH which shows the photocatalyst is active in the presence of light only. So, by this method we can regenerate NADH or NADPH from the NAD^+ or $NADP^+$ respectively [10]. The NADH or NADPH regenerated have 3 isomers i.e 1,4 NADH, 1,2 NADH, 1,6 NADH in which only the 1,4 NADH is enzymatically active whereas, 1,2 NADH and 1,6 NADH are enzymatically inactive. Therefore, the 1, 4 NADH is the NADH which is used in the further industrial applications for example, in reduction of carbon dioxide. NADH is further used to treat diseases such as CFS (Chronic fatigue syndrome), Alzheimer's disease and dementia.

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