Title:	Solar-fuels and valorized organic products from biomass- based precursors: Boosting bio- chemical economy through carbon nitride based photocatalytic systems
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Keywords:	Solar-fuels Organic Products
Issue Date:	Oct-2022
Publisher:	IISER Mohali
Abstract:	Abstract Expeditious fossil fuels consumption by modern society setting up a deep concern for the global energy crisis in the near future. Huge energy demand generally relies on large-scale depletion of non-renewable fossil fuels. In addition, extensive mining and burning of non-renewable sources (fossil fuels) apparently piling-up the carbon dioxide (CO 2) level into the atmosphere which is an alarming call for global warming and has an adverse impact on the environment. Therefore, it is urgent to mitigate an anthropogenic emission of CO 2 in the atmosphere and to hunt for alternative renewable fuels to fossil fuels. Asserting the production of H 2 fuel (green fuel) via proton reduction and CO 2 reduction to high value CO (viably utilized in Fischer-Tropsch process) via renewable solar light assistance provides an exceptional platform to solve the energy-crisis impact globally. Generally, sacrificial agents like tri- ethanolamine (TEOA), alcohols, amines and acids are commonly employed as electron donors to trap the holes in order to promote the above mentioned reactions (proton reduction to H 2 and CO 2 reduction). However, this strategy has some drawbacks like undesirably wasting the energy of holes, offering not only the generation of low value or waste oxidation products but also lowering the chemical economy overall. In that sense, the oxidation of an abundant biomass based organic fractions to value-added chemicals in synergy with the proton reduction to H 2 and CO 2 reduction to CO under the solar irradiation could be a green and sustainable route to boost the bio-chemical economy. Therefore, in the present thesis, we focuses on solar driven production of fuels (H 2 and CO) and oxidation of biomass based precursors to high value-added fine chemicals by using mesoporous carbon nitride based photocatalytic systems. In the first study, we demonstrated photocatalytic oxidation route of renewable biomass furfural (FUR) to produce industrial feedstocks maleic anhydride (MAN) and 5- hydroxy-2(5H)-furanone (HFO) under simulated solar light (AM 1.5 G) using molecular oxygen (O 2) asterminal oxidant and mesoporous graphitic carbon nitride (SGCN) as photocatalyst. SGCN showed an excellent photo-conversion (>95%) of FUR with 42 % and 33 % selectivity of MAN and HFO, respectively. Moreover, along with extensive mechanistic study, this work describes an effective way to utilize both photo-induced electrons (e -) and holes (h +) to strategize not only the FUR oxidation but also the oxidation of biomass based furan derivatives towards high selectivity products under the solar light irradiation. In our next study, we demonstrate the dual functional photoredox process by effective utilization of electrons (e -) and holes (h +) for simultaneous H 2 fuel production and organic transformation of biomass based furfuryl amine to corresponding imines. Herein, we highlighted a photocatalytic acceptorless dehydrogenation (PAD) of biomass based furfuryl amine to corresponding imines coupled with H 2 evolution over mesoporous carbon nitride (SGCN) photocatalyst by using non-noble metal (Ni) as co- catalyst. As synthesized 2 wt. % Ni@SGCN photocatalyst showed photocatalytic activity (visible light) for furfuryl amine valorization with H 2 generation rate of 5.03 µmol h -1 g -1 along with 12.5 % conversion to imine with >99 % selectivity in 6 h. In an advancement to the above highlighted work, we developed urea derived carbon nitride (UCN) and Nb 2 O 5 based dual-functional photocatalytic reaction system for an efficient H 2 evolution and multifarious carbon fuel additive production from biomass derived ethanol in a synergistic manner. The fabricated Pt/UCN/Nb 2 O 5 photocatalyst showed the co-production of H 2 and 1, 1, di-ethoxyethane (DEE) as fuel additive from biomass-derived ethanol solution via photocatalytic dehydrogenation (PD) pathway. As a consequence, the photo-performance of the Pt/UCN/Nb 2 O 5 -(2) catalyst was scrutinized for DEE (506.6 µmol h -1 g -1) and H 2 (558 µmol h -1 g -1) production initially for 6 h under solar simulator irradiation. Additionally, apparent quantum yield (AQE) for H 2 production (400 nm) and solar-to- hydrogen (STH) conversion efficiency were estimated to be 2.18 % and 0.04 % in 6 h, respectively. In this sense, the current study provided an excellent strategy for the fabrication of photocatalysts to offer dual-functional redox process for the realization of H 2 and value-added chemicals from biomass fractions in order to boost the chemical economy and in turn achieving the sustainable synthesis. In addition to environmental crisis, the global energy issues could further be taken care by converting CO 2 to value added products/fuels. To address this challenge, in our next study, we strategized metal-free fullerene-carbon nitride (C 60 /g-C 3 N 4) composite for CO 2 photoreduction to CO (fuel) integrated with biomass based alcohol oxidation for the first time. To the best of our knowledge,no reposts have shown this coupling strategy for CO 2 photoreduction to CO production in synergy with biomass based alcohols oxidations. Immensely, we observed that among all composites, 5-C 60 /TUCN composite showed highest CO 2 to CO conversion efficiency integrated with para-methoxybenzyl alcohol (p-MBA as lignin biomass model substrate) oxidation under solar simulated light with an exciting CO production rate as 9.80 mmol h- 1 g -1 and p-MBA oxidation rate as 1.60 mmol h -1 g -1 . Thus, the current study insights excellent proof-of-concept to fabricate metal-free photocatalytic systems to offer dual-functional for up cycling CO 2 and biomass synergistically into solar fuels and fine chemicals, featuring in sustainable approach to boost the overall (bio)-chemical economy. Overall, the promising advantage of dual redox process by effective utilization of photogenerated e - and h + for solar fuels production and biomass oxidation, respectively under solar light irradiation has been demonstrated. Moreover, governing a sustainable pathway to harvest the renewable solar light for efficient chemical economy through abundant biomass and their derivatives is an exciting research to be explored in a large manner.
URI:	http://hdl.handle.net/123456789/5275
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