Title:	Solar-driven fuel production integrated with biomass valorization over heptazine based photocatalytic systems: Could sunlight be the fossil fuel of the future?
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Abstract:	Fossil fuels pervade the modern human life in every aspect. Based on 2015 annual production and known reserves, it is estimated that the coal reserves may last up to next ~109 years. In addition, natural gas reserves may last up to next ~ 48 years and oil reserves may last up to next ~46 years. Unfortunately, 80 % of global energy supply still depends on fossil fuels and by 2050, we need to double our global energy supply. In addition, the use of non-combusted fuel becomes the major source for the rise of fossil fuel demand towards 2035 in Global chemical sector. As a result, the depletion of fossil fuels not only pose challenge to the future global energy sector but also the future global chemical sector. Even though new fossil reserves may be discovered sooner or later but their consumption further increases the atmospheric CO2 concentration, which will be a serious environmental concern. Therefore, the future global energy and chemical sector should be independent of fossil fuels. The photosynthesis in plant is the nature's finest example which provides key in solving the present fossil fuel crisis. In this line, the artificial photosynthesis which mimics the natural photosynthetic process and produces H2 or H2O2 by water or oxygen reduction coupled with non-edible biomass oxidation to fine chemicals could be a game changer. Furthermore, the carbon-free solar fuels (H2 and H2O2) and biomass derived fine chemicals could be the holy grail that makes the future global energy and chemical supplies more resilient and completely independent of fossil fuels (Figure 1). In this regard, development of industries to harvest natural sunlight rather than fossil fuels to produce carbon-free solar fuels coupled with fine chemicals will be the main pillars of sustainable development. Figure 1: Sunlight could be the fossil fuel of the future: A visible active photocatalyst can harvest sunlight to produce fuels (H2 & H2O2) and fine chemicals from water and biomass. Therefore, present thesis focuses on solar driven synthesis of carbon-free solar fuels coupled with non-edible biomass oxidation to high value fine chemicals by using Heptazine based photocatalytic systems. In our initial study, we demonstrated a win-win approach to produce H2 coupled with biomass derived 5-(Hydroxymethyl) furfural (HMF) oxidation to more valued selective platform chemical, 2,5-Diformylfuran (DFF) under visible light using sol-gel derived porous carbon nitride (SGCN) for the first time. Simultaneously, 12 □mol/h/m2 of H2 was obtained with the DFF yield of 13.8 % with >99 % selectivity after 6 h under visible light. The selectivity of DFF was maintained >99 % even after longer runs (48 h) with improved DFF yield 38.4 %. In addition, 6.2 □mol/h/m2 of H2 along with the DFF (7.2 % yield) were produced under natural sunlight after 6 h. Thus, this study describes an effective way to utilize both photogenerated electrons and holes for the simultaneous H2 production by water splitting and biomass derived HMF oxidation to DFF, respectively under natural sunlight. In our next study, we demonstrated a novel approach to synthesize a true oxygen linked Heptazine polymers (OLHP) by introducing cyameluric acid as a new precursor under inert atmosphere. The O-linkage improved the hydrogen evolution rate of OLHP-550 by 41 folds higher than that of g-CN (commonly known as g-C3N4 with typical NHx linkage). Moreover, the OLHP-550 produced 272 □L of H2 after 7.5 h under natural sunlight. Thus, this study describes a constructive role of precursor selection to improve the catalytic properties (hydrogen evolution) of final polymer. In another study, we demonstrated through a one shot two birds strategy to produce H2O2 along with biomass oxidation to fine chemical under visible light using CNO for the first time. The CNO shows 2 times higher H2O2 production compared to the bench mark g-CN under simulated sunlight. The superior activity of CNO over g-CN attributes to its C-OH/C-O-C bonds, which selectively promotes 2-electron oxygen reduction. Further, 45 □mol/g of H2O2 was obtained along with the DFF yield of 47 % after 24 h under visible light for the first time. Moreover, 34 □mol/g of H2O2 was obtained with 51 % yield of DFF after 8.5 h under natural sunlight which shows a promising route towards the production of liquid based solar fuels. In the next study, a metal-free heptazine-based porous polymeric network (HMP-PPR) was developed for the first time. The HMP-PPR showed wide UV-Vis absorption which catalyzes the production of H2O2 under simulated and natural sunlight through oxygen 2-electron reduction process. The HMP-PPR stably generates about 750 □mol/g of H2O2 over propan-2-ol (IPA) after 24 h under simulated sunlight. Further, under natural sunlight, it produces 151 □mol/g of H2O2 from pure water in 4 h. The HMP-PPR further produced about 323 □mol/g of H2O2 along with 4-Methoxybenzaldehyde after 24 h. In another study, tris (2-aminoethyl) amine (AA) and hydrazine (HZ) were used as linkers to synthesize heptazine based HP-AA and HP-HZ frameworks, respectively. The Conduction Band (CB) was found to be at -0.73 and -0.35 V (vs Ag/AgCl) for HP-AA and HP-HZ, respectively. Based on the appropriate conduction band position, the hydrogen evolution and benzylamine homocoupling was only observed for HP-AA rendering HP-HZ photo-inactive. To the best of our knowledge, this is the first study which explored the band structure tuning driven by the utilization of soft linkers in the heptazine-based frameworks. We believe that, such studies will be beneficial to advance the process of design strategies in heptazine-based polymeric frameworks. In summary, solar driven, especially natural sunlight could be the "fossil fuel of future", only when we utilize both photo-generated holes and electrons effectively to produce fuels coupled with fine chemicals by developing visible light active photocatalysts with appropriate band positions for targeting the sustainable benign process.
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