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Title:	Photocatalytic upgradation of Biomass-derived precursors to Fuels and value-added Chemicals: A roadmap for Sustainability
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Abstract:	<p>The expansion of industrialization to meet the ever-increasing energy demand for the growing population has burdened the limited fossil fuel sources. These readily available hydrocarbon based combusted fuel for energy and non-combusted fuel for chemicals took millions of years, which could approximately last only for the next 50 –100 years unless new reserves being found. In addition to its confined reserves, the extensive consumption of these non-renewable sources has increased atmospheric CO₂ concentration leading to serious environmental crisis. Taking into consideration the current global energy supply dependency on fossil fuels to fulfill vast energy demand, the shift towards renewable and abundant sources for energy and chemical supply is imperative. Solar to fuels or photon energy to chemical energy via mimicking natural photosynthesis provides key in solving the present fossil fuel crisis. Besides sunlight as green energy source, non-edible biomass serves as clean and copious chemical feedstock to generate liquid fuels and commodity chemicals. Moving forward in this direction by integrating light energy and chemical feedstock over a photocatalytic system to produce green fuel and fine chemicals could be a game changer towards sustainable development. Therefore, present thesis focuses on deployment of different semiconducting materials with nano dimensional structures and the light based induction of charge carriers with their effective consumption for redox transformations. The red-ox potentials of photogenerated excitons were utilized for the upgradation of non-edible biomass-derived precursors to renewable fuels and high value-added products under benign conditions. In our first work, the photocatalytic oxidation of alicyclic hydrocarbon based alcohol i.e. cyclohexanol to its corresponding aldehyde (cyclohexanone) using molecular O₂ as is demonstrated. The oxidation occurred as combined effect of photogenerated charge carriers (h⁺ and e⁻) over O- deficient WO_{3-x} nanorods and carbon nitride (g-CN) nanosheets under simulated solar light (AM 1.5 G). The synthesized 1D-2D interfacial system with ~3 wt.% Pd as cocatalyst showed improved charge separation and migration property resulted 90% yield of cyclohexanone – a polymer feedstock for caprolactum and adipic acid. Thus, the present study provides an effective strategy to alter band potentials by surface modifications and to separate charge carriers across the interface for superior activity. In our next work, we demonstrated the activity of multiphasic TiO₂ nanoparticles in photocatalytic hydrogenation of 5-hydroxymethylfurfural (HMF) – a biomass-derived platform chemical to 2,5-bis (hydroxymethyl) furan (BHMF) – a resin and bio-feedstock, without additional reductant. In this work, 30% yield of BHMF was achieved after 24 h over P25 TiO₂ in 400 W Xenon at 25 ° C, simultaneously with the production of 4-anisaldehyde – an intermediate chemical for pharmaceuticals and perfumery. Thus, this study together put forwards the active role of different phases of TiO₂ and describes the effective way to utilize both photogenerated holes (h⁺) and electrons (e⁻) for simultaneous oxidation and reductive hydrogenation, respectively. To further improve the catalytic efficiency of P25 TiO₂ and its activity in visible range of solar spectrum was further improved by coupling UV active TiO₂ nanoparticles with a visible light active semiconductor i.e. CdS nanorods. The intimate interfacial contact between the two semiconducting systems instigated the photogenerated electrons on CdS surface to migrate towards catalytic sites of P25 TiO₂. The final heterostructure resulted in 95% BHMF yield after 12 h reaction time under visible light at 25 ° C simultaneously yielding 32 % of vanillin – a flavor additive. Thus, the current study presents the strategy to improve photogenerated charge carriers separation in heterostructure resulting in excellent activity in visible light without external reducing agents, which helps in boosting the chemical economy. In our next study, we demonstrated the oxidative acetalization of furfural (FFaL) – a platform chemical derived from hemicellulose, to 2-furyl-1, 3-dioxolane (FD) – a fuel additive over ZnIn₂S₄ in visible light at 25 ° C. The 2D layered structure aggregated into flower-like microspheres of ZnIn₂S₄ resulted cyclic acetal i.e. FD yield of 92% after 4 h in oxygen atmosphere. The detailed study of photogenerated charge carriers utilized to carry out the acetalization suggested the prominent role of holes (h⁺) in catalyzing the reaction. Once more, simple reaction conditions without additional redox reagents put forwards the current system as sustainable route to upgrade biomass-derived precursors into high-value chemicals. In our last study, the visible light active ZnIn₂S₄ nanosheets were grown over high- surface area TiO₂ nanorods to develop 1D-2D interface with enhanced charge separation and migration properties. The synthesized heterojunction successfully transformed levulinic acid (LA) – a biomass-derived precursor into γ-valerolactone (GVL) – a biofuel. The current system showed excellent conversion activity of 87% in 3 h under benign reaction conditions using simulated solar light (AM 1.5 G). Thus the present study reports the easy way of integrating solar energy and chemical feedstock as promising route towards sustainable production of liquid biofuel. In summary, the implementation of different semiconductors exploiting their band gap and band positions to carry out organic transformations is a promising approach towards green conversions. Overall, the effective utilization of redox potentials of photogenerated charge carriers put forward a renewable route for commodity chemicals and biofuel production by maintaining the chemical economy.</p>
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