Titania-based heterogeneous photocatalysis for the selective oxidation of biomass-derived platform chemicals

Author: Ayesha Khan

Date: 29th September, 2021

Summary

Titania, as a heterogeneous photocatalyst has a significant potential for the conversion of biomass to value-added products. However, it is often unselective in organic oxidation reaction due to the generation of highly active oxidizing species, which over oxidizes the substrate under high energy UV radiation. On the contrary, titania-based visible light-driven photocatalysis for the selective oxidation of biomass-derived platform chemical is considered to be economical and environmentally benign approach. This thesis primarily focused on the visible light activation of titania for its application in the photocatalytic selective oxidation of biomass-derived platform chemicals into value-added products. Two approaches were employed for the visible light activation of titania for the selective oxidation of biomass-derived platform compounds i.e. i) Ligand-to-metal charge transfer (LMCT)-sensitization ii) Preparation of nanocomposites of titania and carbon materials. For LMCT-sensitization, titania nanoparticles were synthesized via sol-gel and hydrothermal method, subsequently sensitization of titania was achieved through the formation of visible light absorbing LMCT-complex on the titania surface by the adsorption of platform molecule, 5-hydroxymethylfurfural (HMF). The resulting LMCT-complex enabled the oxidation of HMF (59% conversion) to an industrially relevant compound 2,5- diformylfuran (DFF), with high selectivity (87%) under visible light (λ = 515 nm). In an attempt to improve the visible light activity of titania through nanocomposite formation, first, a set of chitosan-lignin (CL) composites have been synthesized via a hydrothermal method by varying the proportion of chitosan and lignin. Afterward, the as-prepared CL composites have been coupled with titania (T) to prepare a nanocomposite (T/CL) through sol-gel and hydrothermal approach. The test reaction used to assess the photocatalytic activity of T/CL

nanocomposite under visible light (λ = 515 nm) is the selective oxidation of benzyl alcohol (BnOH) to benzaldehyde (Bnald). A representative nanocomposite, 75T/CL(25:75) exhibited excellent selectivity for Bnald (100%) at moderate BnOH conversion (19%) under visible light. On the basis of XPS measurements, it is suggested that the T/CL nanocomposites activity under visible light may ascribed to the doping of nitrogen into titania framework from chitosan. The current findings, therefore suggest that visible-light driven heterogeneous photocatalysis employing abundantly available titania holds significant potential for the valorization of biomass-derived platform compounds via selective oxidation.