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Multifunctional NiO/Ti^{3+}–TiO_2 for concurrent water reduction and glycerol oxidation to value added products by sunlight driven photocatalysis†

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The present work describes the synthesis of bifunctional-mesoporous-self-doped Ti^{3+} containing NiO/TiO_2 photocatalysts for concurrent utilization of e^- and h^+ to produce H_2 and value-added products (VAPs), respectively, from aqueous glycerol. UV-vis diffuse reflectance results and band gap analysis revealed an improved light absorption due to integration of Ni^{2+} with Ti^{3+}/TiO_2. Various electrochemical, PL and TRPL spectral analyses demonstrate p–n heterojunction formation between NiO and Ti^{3+}–TiO_2, which enhances charge separation and helps in achieving improved activity. HRTEM analysis of NiO/Ti^{3+}–TiO_2 nanocomposites revealed that NiO is highly dispersed on TiO_2 with interfacial heterojunctions between them. XPS results demonstrate the partial reduction of Ti^{4+} to Ti^{3+} and Ni–Ti synergetic interaction in NiO/TiO_2 to form NiO/Ti^{3+}–TiO_2 nanocomposites. EXAFS studies show that the Ni–O bond distance is similar to that of $NiTiO_3$ suggesting electronic integration of components of the photocatalyst by forming a Ni^{2+}–O–Ti^{3+}/Ti^{4+} lattice network. Ni^{2+}/Ti^{3+}–TiO_2 nanocomposites as a bifunctional photocatalyst exhibited significantly enhanced activity in H_2 production and conversion of glycerol to VAPs, namely, glycolaldehyde, 1,3-dihydroxyacetone, and formic acid; formation of these products highlights not only oxidation, but also C–C cleavage of glycerol. The NiO/Ti^{3+}–TiO_2 photocatalysts fabricated in thin film form displayed higher photocatalytic efficiency than their powder counterpart. Among NiO/Ti^{3+}–TiO_2 nanocomposites NiT-3 exhibits the highest H_2 yield at 15.62 mmol h^{-1} g^{-1}, which is 38 times higher than that of bare TiO_2. The enhanced photocatalytic activity is ascribed to the high charge carrier density, the synergistic interaction between Ni^{2+} and Ti^{3+}–TiO_2, formation of a p–n heterojunction at the interface between NiO and Ti^{3+}–TiO_2 and effective utilization of charge carriers for redox reactions.

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1. Introduction

Hydrogen is considered as a promising energy source due to its high combustion energy and environmental friendliness, which make it a viable option for addressing the global energy and environmental crises.[1,2] However, the current fossil fuel-based thermochemical methods such as hydrocarbon reforming, plasma reforming, coal gasification, and hydrocarbon pyrolysis for the hydrogen production process generate large amounts of carbon products.[2–4] In this context, photocatalytic and photoelectrocatalytic carbon-free hydrogen production by water splitting by utilizing the highly abundant natural resources water and sunlight is highly attractive and a promising alternative to hydrogen production from fossil fuel-based processes.[2,5] However, the large-scale practical application of the photocatalytic hydrogen evolution reaction (HER) was limited mainly due to the sluggish oxygen evolution reaction (OER) and high electron–hole recombination rate.[6] Coupling of the photocatalytic HER process with selective conversion of

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† Electronic supplementary information (ESI) available: Tables for XPS parameters, N_2 adsorption–desorption isotherms, pore size distribution patterns, FESEM, SEM-EDS, XPS spectra, structural parameters obtained from EXAFS analysis, average lifetime, photocurrent measurements, stability of the photoelectrode, EIS parameters, CV at different scan rates, C_{dl} and ECSA values, MS plots, post-catalytic measurements, comparison of photocatalytic activity, AQY, product analysis of glycerol oxidation, calculation of the e^-/h^+ ratio, ^1H NMR spectra, influence of addition of scavengers, plausible reaction pathway and comparison of activity with that reported in the literature. Short video of the continuous H_2 production from the surface of the thin-film [(Video V1) (.MP4)]. See DOI: https://doi.org/10.1039/d4ta06910b

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