



Unveiling the role of bisulfide in the photocatalytic splitting of H₂S in aqueous solutions

Giovanni Palmisano

Khalifa University, PO Box 54224, Abu Dhabi, UAE

Abstract:

Aqueous anaerobic photocatalytic conversion of hydrogen sulfide was performed in the presence of a Pt-decorated N-doped multiphase titanium dioxide grown on graphene, to investigate the mechanism of hydrogen generation. The catalyst has doubled the production rate of H₂ comparatively to the benchmarked catalyst (Pt-decorated TiO₂ P25). The effect of bisulfide ion (HS⁻) concentration in the overall performance was investigated at constant pH. An increase in the pseudo-zero order rate constant for hydrogen generation was observed with the increase of HS⁻ concentration, until a critical value of 0.029 mol/dm³, after which a steady decline in rate took place down to a negligible activity. The latter was attributed to adsorption competition between HS⁻ and S₂⁻; accordingly, a possible mechanism and kinetic model was proposed and matched to the experimental data. Evidence from XPS highlighted a significant amount of sulfur adsorbed on the catalyst surface when the concentration of sulfide and bisulfide ions in the starting reactant solution was high. This adsorbed sulfur species produced a deactivation of the catalyst under certain experimental conditions. Furthermore, UV-Vis DRS analysis of catalyst after reactivity test confirmed the formation of an adsorbed complex tending to hinder light from reaching catalyst surface when the system had been irradiated for several hours. Interestingly, after washing the spent catalyst with deionized water, sulfur was no longer detected, testifying the reversibility of the catalyst poisoning due to sulfur-containing species. On the other hand, experiments performed at constant HS⁻ concentration, and increasing pH's did not reveal any strong correlation. Thus, it can be inferred that hydrogen cations are not main actors in the photocatalytic production of hydrogen and bisulfide ions are the main chemical species participating in the rate-limiting steps in this process. In the second part of the study, the higher activity observed under the home-made cata-



lyst was investigated by extensively characterizing both catalysts using Transmission Electron Microscopy (TEM/EDS), UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS), X-ray Photoelectron Spectroscopy (XPS), X-ray Diffraction (XRD), Raman Spectroscopy and Photoluminescence (PL).

Biography:

Giovanni Palmisano is an Associate Professor of Chemical Engineering at Khalifa University, where he leads the Photocatalysis and Reaction Engineering Lab.

Publication of speakers:

1. Unveiling the role of bisulfide in the photocatalytic splitting of H₂S in aqueous solutions
2. Hydrogen production upon UV-light irradiation of Cu/TiO₂ photocatalyst in the presence of alkanol-amines
3. Alkaline treatment as a means to boost activity of TiO₂ in selective photocatalytic processes
4. Highly stable defective TiO_{2-x} with tuned exposed facets induced by fluorine: Impact of surface and bulk properties on selective UV/visible alcohol photo-oxidation
5. Multilayer thin film structures for multifunctional glass: Self-cleaning, antireflective and energy-saving properties

Frontiers in Catalysis and Chemical Engineering, Amsterdam, March 23-24, 2020

Citation: Giovanni Palmisano Unveiling the role of bisulfide in the photocatalytic splitting of H₂S in aqueous solutions; March 23, 2020; Amsterdam, Netherlands.