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كليه العلوم – قسم الكيمياء



Development of Novel Solar Light-Activated Photocatalysts for Clean Energy Production and Degradation of Emerging Contaminants

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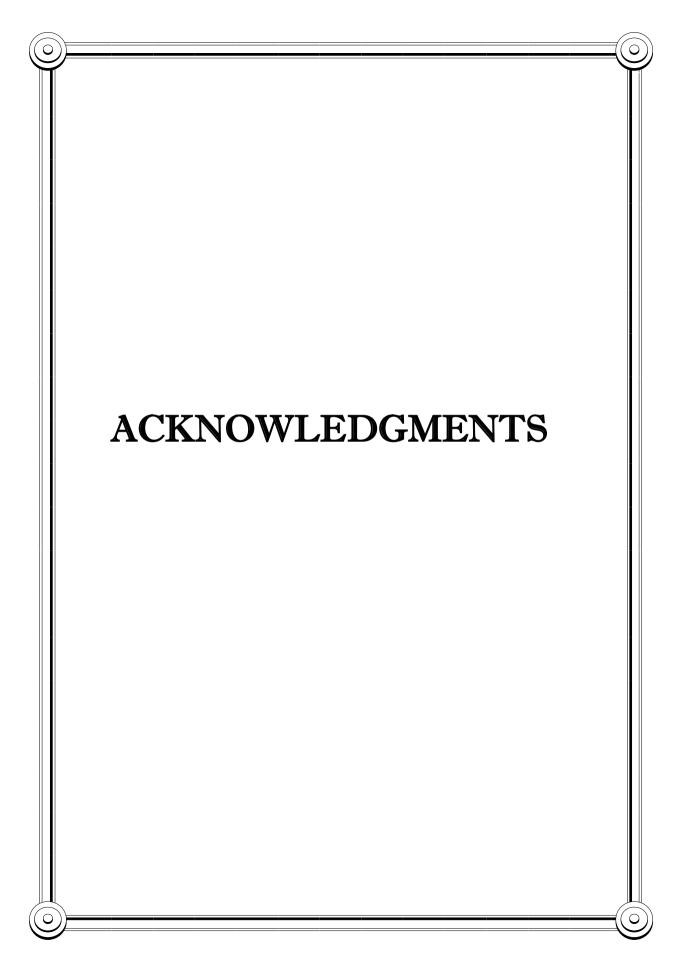
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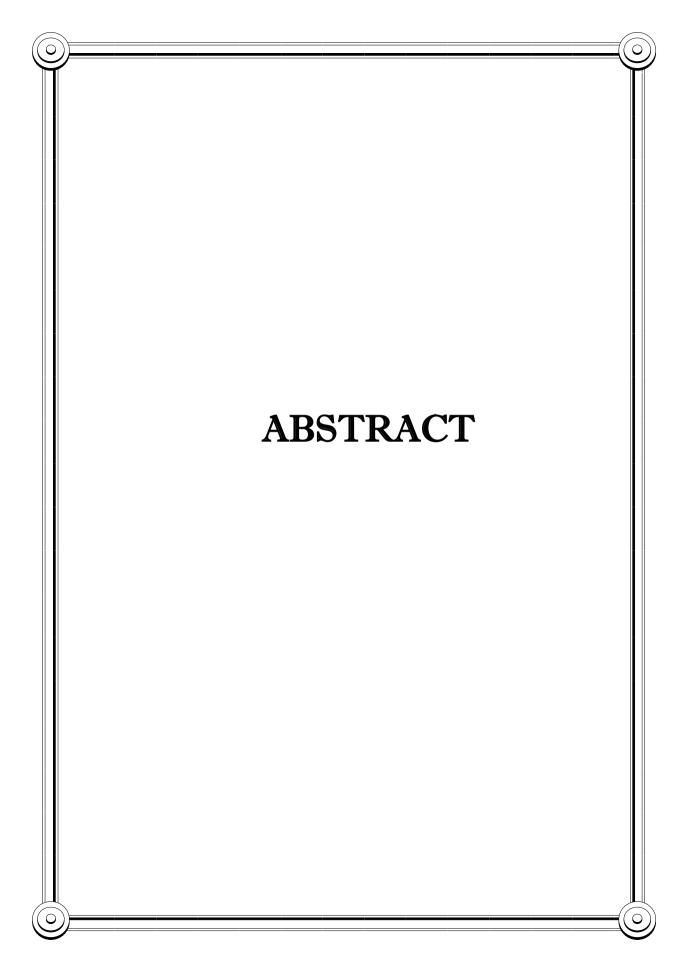
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II



Development of Novel Solar Light-Activated Photocatalysts for Clean Energy Production and Degradation of Emerging Contaminants

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ABSTRACT

Energy and water crisis are two of the most serious threats to human life and property worldwide. Energy supply depends on water. Water supply depends on energy. The interdependency of water and energy is set to intensify in the coming years, with significant implications for both energy and water security. Each resource faces rising demands and constraints in many regions as a consequence of economic and population growth and climate change.

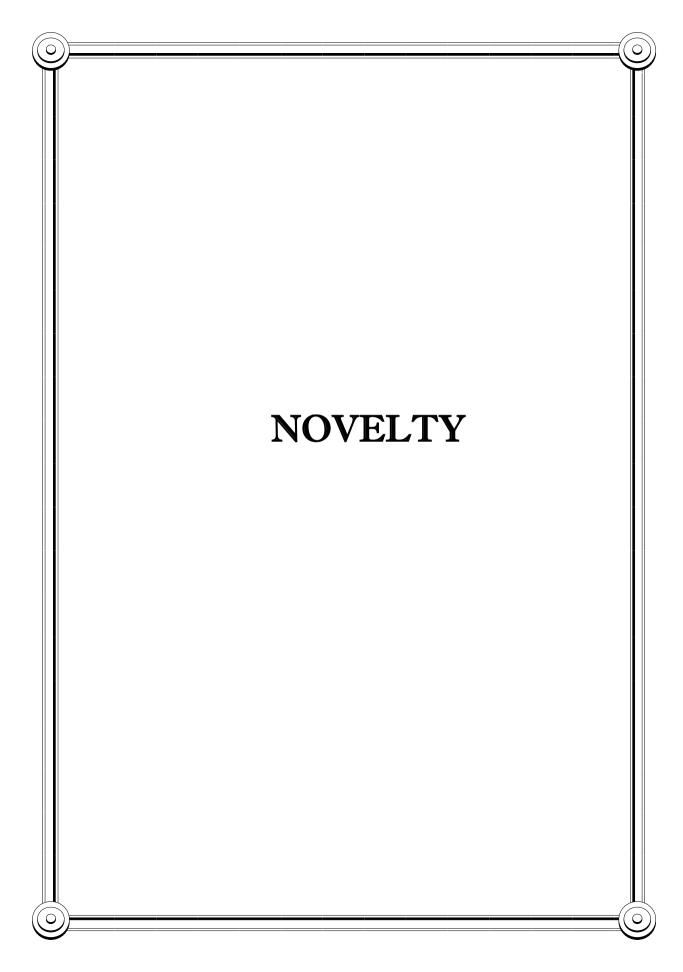
Hydrogen (H₂) has been broadly suggested as an alternative fuel to overcome energy shortages and environmental pollution because of its fascinating advantages, i.e., being renewable, eco-friendly, clean, recyclable, and with high-energy density. However, the present technologies (i.e., fossil fuel-based and renewable-based methods) used for hydrogen production are facing great challenges to deal with global sustainable development because they might be environmentally toxic, expensive or requiring external energy. Future sustainable energy scenarios require improved access to renewable energy sources and thus help to reduce the carbon footprint of the energy sector.

Over one billion people worldwide lack access to safe drinking water, which leads to many waterborne diseases and deaths. According to World Health Organisation (WHO), half of the world's population would be facing water shortage by 2025. Water polluted by emerging pollutants like cyanotoxins and pharmaceutical products has lethal effects on both the environment and living organisms. To address these threats, various technologies, such as adsorption, filtration, flocculation, sedimentation, coagulation, disinfection, chemical oxidation, chlorination and microbial degradation, have been developed to remove emerging from the water. However, these technologies are not effective from the viewpoint of cost and process efficiency. Moreover, either toxic sludge (solid waste with metabolites/byproducts) or concentrated wastewater is simultaneously created that requires further treatment. The dream concerning the implementation of a solar photocatalytic system combining the conversion of aqueous organic pollutants into value-added fuels, i.e., H₂, is still far from being realized because of technical, materials and reaction-mechanistic related issues. Titania (titanium(IV) oxide, TiO₂) is probably the most widely investigated due to high activity, stability, abundance, and low toxicity, but its application is limited due to charge carriers' recombination and inability of visible light (vis) absorption.

In this thesis, binary-phase (anatase/brookite) mesoporous TiO₂ (bare and C-N-S tri-doped), 2D S-doped mesoporous g-C₃N₄, and direct Z-scheme of 2D/2D mesoporous S-doped g-C₃N₄/Bi₂WO₆ photocatalysts were simply synthesized and were characterized using advanced techniques. The photocatalytic activities of as-synthesized photocatalysts were evaluated by photocatalytic H₂ generation, overall water splitting, and degradation of emerging pollutants (DCF and MC-LR), as well as simultaneous H₂ evolution and photodegradation of pollutants under UV, UV-vis and vis irradiation. The

results revealed that the photocatalytic H₂ evolution and degradation of organic pollutants under UV-vis and UV-A irradiation were boosted using bare mixedphase (anatase/brookite) mesoporous TiO₂ photocatalyst, compared with single-component TiO₂ (anatase and brookite) and P25-TiO₂. This remarkable activity could be attributed to an unique structure (mixed-phase and mesoporous), efficient light harvesting (bandgap narrowing), higher specific surface area, transfer of charge carriers between anatase and brookite phases (heterojunction type II), shallow electron traps, and possible interparticle charge transfer excitation (ICTE). Moreover, C-N-S tri-doped binary phase (anatase/brookite) mesoporous TiO₂ photocatalyst showed an enhanced photocatalytic activity towards H₂ generation and organic pollutants degradation under vis irradiation, compared with bare TiO₂ because of nonmetal doping. Compared with bulk g-C₃N₄, the 2D S-doped mesoporous g- C_3N_4 photocatalyst displayed a boosted photocatalytic activity for H_2 evolution and organic pollutants degradation under vis irradiation because of S-doping, 2D mesoporous structure, high surface area, high light-absorption ability, and high efficiency of electron-hole separation. Among the as-synthesized photocatalysts, the direct Z-scheme (S-doped g-C₃N₄/Bi₂WO₆) photocatalyst exhibited the best photocatalytic activity towards H₂ generation (co-catalystassisted and co-catalyst-free H₂ evolution), and overall water splitting, as well as degradation and mineralization of DCF and MC-LR, and simultaneous photocatalytic degradation of pollutants (DCF and MC-LR) and H₂ generation under vis irradiation. This enhanced activity could be greatly assigned to the photogenerated electron's migration from CB of Bi₂WO₆ to VB of g-C₃N₄ according to Direct-Z-scheme.

Keywords: Energy crisis; water crisis; heterogeneous photocatalysis; titania; heterojunction; interparticle charge transfer excitation (ICTE); $g-C_3N_4$; Z-scheme; H_2 ; water splitting; photodegradation.



Novelty of This Thesis:

The novelty of thesis includes the following:

- 1) Template-free hydrothermal method (i.e., simple operation, low cost, and environmentally friendly) was used to synthesize of binary-phase (A/B) mesoporous titania photocatalyst.
- 2) Titanium(III) sulfate ($Ti_2(SO_4)_3$ (i.e., good solubility in water and stability at ambient temperature) was used as a Ti precursor.
- 3) Facile synthesis of C-N-S tri-doped mixed-phase (A/B) mesoporous titania photocatalysts.
- 4) Boosted photocatalytic H₂ generation, as well as complete degradation and mineralization of emerging pollutants under UV, UV-vis and vis irradiation; by the synergistic effect (interparticle charge transfer excitation (ICTE)) of anatase and brookite, and charge carriers' transfer between two phases (type II heterojunction) in binary phase (A/B) TiO₂ photocatalyst.
- 5) Template-free one-pot synthesis of 2D mesoporous S-doped g- C_3N_4 photocatalyst.
- 6) Enhanced photocatalytic H₂ evolution, as well as complete degradation and mineralization of emerging pollutants under vis irradiation over 2D mesoporous S-doped g-C₃N₄ photocatalyst.
- 7) One-pot synthesis of 2D/2D direct Z-scheme of mesoporous.
- 8) Enhanced photocatalytic H_2 evolution (with using/without using cocatalyst), and overall water splitting, as well as complete degradation and mineralization of emerging pollutants.
- 9) Photocatalytic conversion of aqueous organic pollutants into value-added fuels, i.e., H₂.

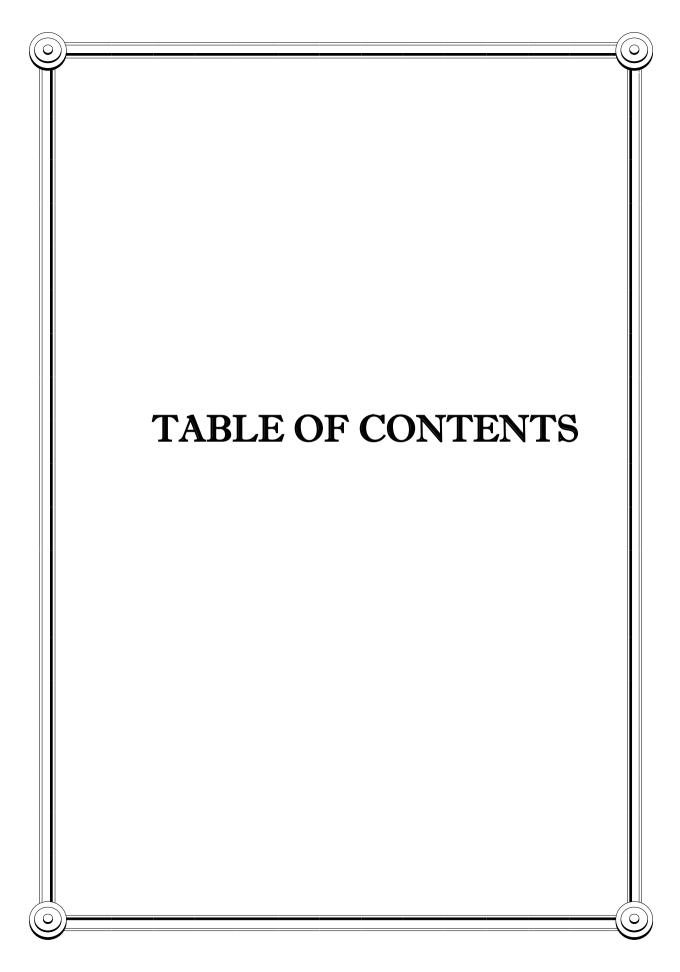


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Chapter 3

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