Title:	Synthesis and Characterization of Semiconductor Nanomaterials for Photocatalytic Hydrogen Evolution
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Abstract:	Photocatalytic water splitting is a holy grail to solve today's energy requirement and environmental problems associated with the usage of traditional fossil fuels and offers an eco-friendly option to store solar energy. Making photocatalytic water splitting efficient and commercially feasible, needs to solve several major problems, one of which is developing photocatalysts. To obtain higher productivity, the photocatalysts should efficiently absorb natural sunlight and separate photogenerated e-h pairs. The exceptional characteristics of photocatalysts at the nanoscale lead to higher activity contrasted to bulk materials. Also, forming heterojunction and solid solutions are efficient ways to increase catalytic activity. In the present thesis, we are concentrating on the preparation of an efficient material for H 2 production through photocatalytic water splitting under natural sunlight. In the first part of the thesis, nano-structured ZnFe 2-x Ga x O 4 (0 ≤ x ≤ 2) solid solution samples are synthesized using the citrate-gel method at 550 °C and investigated their structural and optical properties as well as their photocatalytic hydrogen evolution activity. The formation of solid solution with spinel type structure in the complete range of composition is concluded from the XRD studies and variation of unit cell parameters with composition. The unit cell parameters of the compositions show a systematically decreasing trend with increasing Ga 3+ concentration. The band gap of these solid solutions is tuned from 1.9 to 3.1 eV by increasing the Ga 3+ concentration. The valance band maxima of these nanomaterials are varied from 1.7 to 3 eV while moving from ZnFe 2 O 4 to ZnGa 2 O 4 , respectively. Without any co-catalyst, ZnFe 2 O 4 shows poor catalytic activity for photocatalytic hydrogen evolution from water while its activity enhances with the loading of co-catalyst. Maximum activity is observed with loading 1wt% Pt as co-catalyst. Also, the catalytic activity shows a systematic increasing trend with the increase in Ga concentration in the solid solutions and reaches 0.36 mmol h -1 for ZnGa 2 O 4 nanomaterials. Electrochemical impedance spectroscopic and transient photocurrent measurements also support the observed increasing trend. The lower catalytic activity of ZnFe 2 O 4 has been attributed to the faster e-h recombination due to the lower band gap and inherent oxygen vacancies. The lower oxygen vacancies and segregated ZnO phase observed in Ga substituted ZnFe 2 O 4 samples favor the e-h pair separation and that facilitates the splitting of water. In the second part of the thesis, semiconductor heterojunction photocatalysts are synthesized, i.e., TaON/CdS by a simple precipitation method. The ratio between two viisemiconductors is optimized to obtain maximum hydrogen evolution. XRD and TEM analysis demonstrate the formation of heterojunction between these semiconductors. Among the synthesized catalysts, 3% TaON/CdS heterostructure exhibits the highest hydrogen evolution activity with the H 2 production rate of 7.5 mmol h -1 under natural solar light, whereas the rate is 11 mmol h -1 under the visible light generated by xenon (Xe) lamp without the addition of any noble metal as the co-catalyst. The CdS and 3% TaON/CdS nanomaterials show an AQE of 5.1% and 12.2%, respectively. A combination of Mott-Schottky, UPS and DR UV-visible spectroscopy studies revealed the formation of S-scheme semiconductor heterojunction between these nanomaterials with valance, conduction band positions, i.e., 1.46, -0.78 eV for CdS and 2.19, -0.66 eV for TaON, respectively. These band positions help in efficient e-h pair separation to produce hydrogen from water. In the last part of the thesis, SrTaO 2 N/CdS heterojunction are synthesized by using the coprecipitation method to improve the catalytic activity. SrTaO 2 N/CdS nanocomposite is studied for photocatalytic H 2 generation in both natural sunlight and artificial light (Xe lamp). Among the synthesized nanocomposites, the 5% SrTaO 2 N/CdS heterojunction exhibits the highest H 2 evolution rate of 8.05 mmol h -1 for 5h in the presence of visible light produced by a xenon lamp without utilizing a co-catalyst. This is much higher than that of the catalytic activity shown by SrTaO 2 N and CdS, independently under similar experimental conditions. It is because of the effective e-h pair separation in the nanocomposite due to the S-scheme heterojunction formation between SrTaO 2 N and CdS semiconductors with valance, conduction band positions at 2.27, -0.26 eV for SrTaO 2 N and 1.46, -0.78 eV for CdS, respectively. This composite exhibits hydrogen evolution rate of 8.01 mmol h -1 for 5h under natural sunlight which is a promising step towards practical applications. In summary, the present thesis focus on the synthesis of semiconductor nanomaterials with efficient visible light absorption and separation of photogenerated e-h pairs. Heterojunction formation between oxynitride and CdS leads to efficient photocatalytic hydrogen evolution activity under natural sunlight.
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