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Effective shuttling of photoexcitons on CdS/NiO core/shell photocatalysts for enhanced photocatalytic hydrogen production

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ABSTRACT

Hierarchical structure of NiO immobilized on CdS photocatalyst (CdS/NiO) was synthesized for stable and efficient H_2 production. The catalyst is designed to suppress the photo-corrosion behaviour without affecting catalytic activity of CdS structures having tamarind leaf-like morphology is protected by fabricating thin-layer of NiO. The exterior thin-layer transmits the light into CdS in-turn exciton moved to surface for reaction with adsorbed reactant species. Structural, morphological and optical properties were studied using X-ray diffraction (XRD), ultraviolet-visible light (UV–vis) diffuse reflectance spectra (DRS), high resolution transmission electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS). The results illustrates that synthesized catalyst composed of crystalline CdS/NiO hierarchical structure that absorbs light in the visible spectrum and improved charge carrier separation than CdS or NiO alone. The photocatalytic activity was examined for H_2 generation under visible light irradiation using Xe-lamp as light source. In order to achieve enhanced H_2 production rate amount of NiO loading was optimized and results were found in the following order CdS/NiO > CdS. Under optimal conditions the catalyst showed stable H_2 evolution for 30 h of continuous irradiation. Under optimal conditions catalyst showed visible light to H_2 conversion efficiency of 6.63%.

1. Introduction

Hydrogen (H_2) can be considered as the most promising fuel energy for the future, due to its high calorific value, regarded as a clean and sustainable energy source [1–3]. Though several methods are in practice for H_2 generation, heterogeneous photocatalysis for water splitting has becoming a research hotspot throughout the world due to its simple process, works at ambient conditions and uses eco-friendly resources like water and light energy [4–8]. Among various photocatalysts developed so far, metal sulfides have been proven to be good candidates for H_2 production from water under visible light [9–13]. In particular, CdS has been most commonly studied catalyst, due to its efficient absorption of visible light and having requisite band potentials for photocatalytic H_2 generation [14–21]. Still the stability issues limit CdS for practical applications. Hence many researchers focused on material preparation, with different morphology, crystalline CdS and material modifications with transition metal oxides. There is a significant progress in water splitting on CdS based photocatalysts using solar light, especially in the development of co-catalysts. The photocatalytic properties of CdS materials depend not only on particle size but also morphology [22–24]. For example CdS hollow nanoparticles, nanorods, multipods, quasi-nanospheres, hollow nanospheres, nanoshuttles, nanowires, nanotubes, nanosheets, core-shell nano particles have been reported [25–30], Li et al. [31] reported hierarchical photocatalysts for various applications, including photocatalytic degradation of pollutants, photocatalytic H_2 production and photocatalytic CO_2 reduction. Besides CdS nanostructures, the co-catalysts can also play a vital role in stimulating charge transfer and reducing the recombination of photo-induced charges, thereby enhancing the photocatalytic activity of CdS. The efficient co-catalysts usually contain noble metals (Pt, Au, Rh, RuO_2, etc) [32–35]. But the main issue with them are high cost and not preferable economically. Hence it is necessary to explore non-noble metals to reduce the cost of renewable H_2 production.

Reports on CdS with non-noble metals particularly core/shell type of materials for photocatalytic water splitting are scare. Though CdS is known for good photocatalytic activity, the stability issues are the major concerns. Hence anchoring with core/shell type of materials with transition metal oxides is an efficient technique to overcome the

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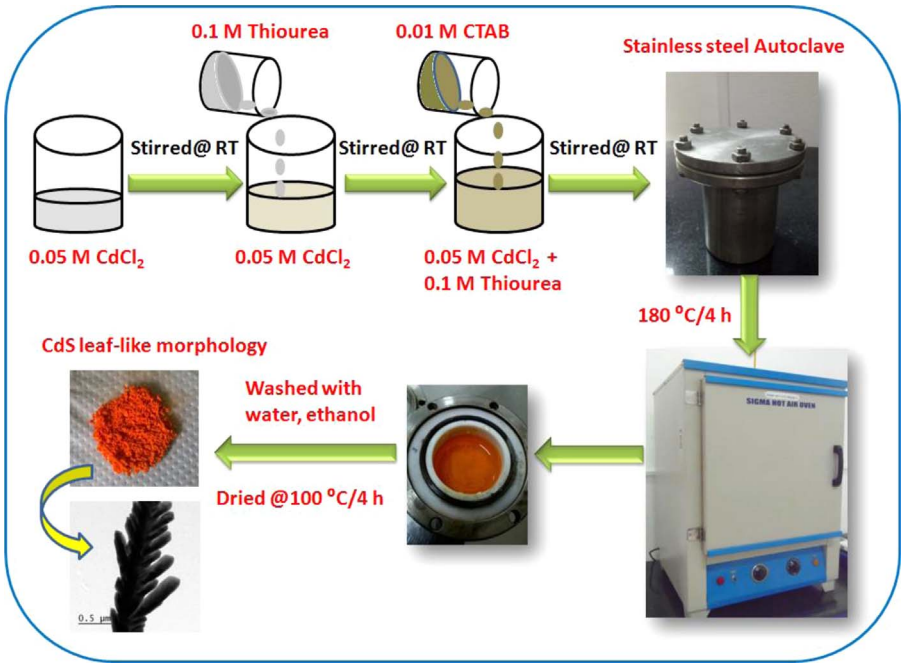
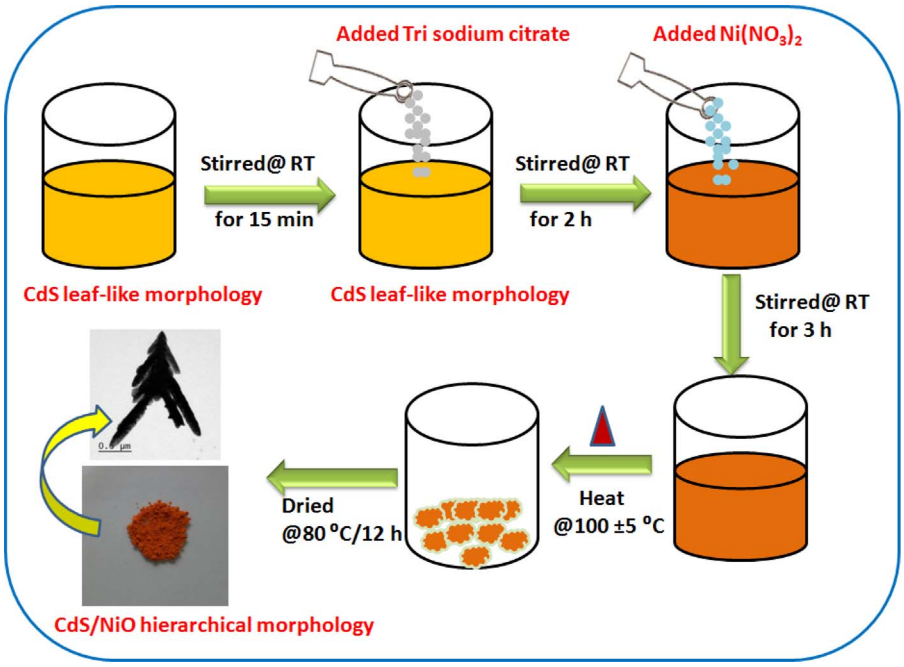


Scheme 1. Schematic representation of preparaion of CdS leaf-like morpholgy.



Scheme 2. Schematic representation of preparaion of CdS/NiO hierarchical photocatalysts.

stability issues. Here the metal oxides covering as a shell with thin layer protects the CdS core from photo-corrosion and thus improves the stability.

Hence in the present work we have prepared CdS tamarind leaf-like structures as a core and coupled with NiO as shell like material to improve the efficiency and stability of the catalyst. Here the NiO shell can protects the CdS core from photo-corrosion, the photo generated charge carriers form CdS can migrate to the surface of the shell and undergo red-ox reactions with minimized recombination. Particularly NiO was found to be used as an excellent co-catalyst to enhance the activity of a photocatalyst. More specifically the selection of NiO is based on its band alignment with CdS as reported in the literature [36]. The conduction band (CB) of CdS (−0.88 eV, pH 0) [4] is in close proximity to the CB of NiO (−0.4 eV, pH 0) [37] which can facilitate efficient charge migration from the CB of CdS to the CB of NiO, thereby minimizing the photo induced charge carriers for improved catalytic activity. The role of NiO was explored based on experimental and characterizations results. The successful utilization of charge carriers from CdS and reduction of H^+ into H_2 was studied through plausible reaction mechanism.

2. Materials and methods

2.1. Chemicals and reagents

All the chemicals used for the present work are Analytical Grade and used as received without further purification. The details of the Chemicals and Catalysts used are given below. Cadmium chloride monohydrate ($CdCl_2.H_2O$), Nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$), Tri sodium citrate dihydrate($C_6H_5Na_3O_7.2H_2O$) were