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Nanohybrid MoS_2-PANI-CdS photocatalyst for hydrogen evolution from water

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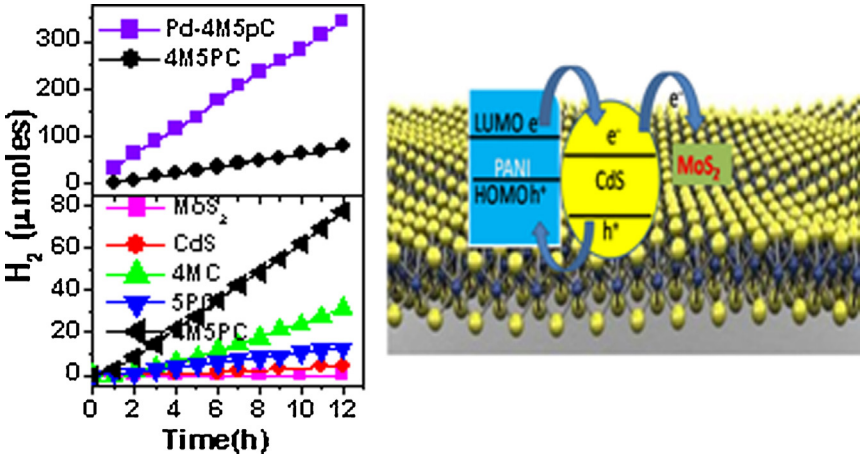
HIGHLIGHTS

- MoS_2-PANI-CdS nanohybrid shows enhanced photocatalytic activity for H_2 generation.
- Modification of CdS with MoS_2 and PANI leads to increased visible light absorption.
- Increased fluorescence lifetime for the charge carriers is observed for composites.
- Increased photocurrent response is observed for composite.
- The hybrid catalyst is found to be stable for repeated cycles of experiment

GRAPHICAL ABSTRACT



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ABSTRACT

A ternary nanohybrid material, MoS_2-PANI(polyaniline)-CdS, exhibits enhanced photocatalytic activity for hydrogen generation from water compared to single phase CdS, MoS_2-CdS and PANI-CdS composites. The photocatalytic activity increases further when palladium is used as co-catalyst. The modified CdS composite catalyst is found to be stable for repeated cycles of photocatalytic experiments. Increased visible light absorption is seen when CdS is modified with PANI and MoS_2 having a layered structure. Detailed characterization suggests that CdS, PANI and MoS_2 exist as an intimate blend in the composite. Time resolved fluorescence studies show an increased lifetime for the photogenerated charge carriers in MoS_2-PANI-CdS composite. Photocurrent measurements show relatively higher current output for the MoS_2-PANI-CdS sample compared to CdS and other binary composites. The increased photocatalytic activity of the modified CdS catalyst is attributed to the increased visible light absorption, increased photoresponse and increased lifetime of the photogenerated charge carriers promoted by both PANI and MoS_2. In the presence of Pd co-catalyst, interfacial transfer of electrons from the catalyst to Pd occurs, which enhances the separation of charge carriers and provides active sites for hydrogen evolution. Present study provides insights for improving the photocatalytic activity of CdS photocatalyst.

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1. Introduction

Development of photocatalyst, which can effectively utilize solar radiation and generate hydrogen from water, is of immense importance currently. As the solar spectral irradiance is maximum around 600 nm, fabrication of catalyst having bandgap around 2 eV is essential for improving the efficiency of the process. Besides tuning the bandgap, lifetime of the photogenerated charge carriers should be sufficient enough to facilitate their migration to the surface and initiate the redox reaction with water. Cadmium sulfide is a widely studied visible light active catalyst with a bandgap of 2.4 eV [1]. It is a suitable candidate for the application of efficient solar energy utilization. But, the disadvantages like short lifetime of the photogenerated charge carriers and poor photostability of the catalyst have to be overcome for using it for practical applications.

Modification of CdS with other suitable conducting/semiconducting materials can increase the lifetime of the photogenerated charge carriers and can also increase its stability. CdS when modified with PANI exhibits improved photocatalytic activity for hydrogen generation [2]. The enhanced activity is attributed to the electron transfer from PANI to CdS thereby increasing the electron density in CdS. In CdS–PdS-PANI composite, PdS improves the photostability and photocatalytic activity of CdS while PANI can promote the generation of photogenerated electrons and holes and accelerate the transfer of hole from CdS to PdS, preventing the charge recombination [3]. A significant increase in hydrogen evolution rate is observed when CdS-MoS_2 composite was used as photocatalyst [4,5]. The inter-electron transfer between CdS and MoS_2 and the hydrogen activation property of MoS_2 are reported to be responsible for the increased activity. Several composites of CdS like CdS-graphene [6], CdS–ZnO [7,8], CdS–CdO [9,10], and CdS–ZrO_2 [11] show better photocatalytic activity than pure CdS. The increased activity has been attributed to the increased surface area and increased lifetime of the photogenerated charge carriers in these composite systems.

In the present work, we report the photocatalytic activity of a hybrid system of CdS containing a novel combination of conducting/semiconducting materials for hydrogen generation from water using sunlight type radiation. The effect of modification of CdS with both PANI and MoS_2 on the optical and electronic properties as well as its stability is investigated. Photocurrent response and fluorescence lifetime of the photogenerated charge carriers is studied in order to have a better understanding of the electron transfer process occurring in this modified CdS system. The observed photocatalytic activity of different samples is correlated with the photoresponse and the fluorescence lifetime of the charge carriers.

2. Experimental

2.1. Synthesis of CdS and MoS_2-PANI-CdS (MPC) composite

CdS was synthesized by treating aqueous cadmium chloride solution with aqueous sodium sulfide at room temperature under constant stirring. The precipitate obtained was washed with water and ethyl alcohol several times followed by drying in an oven at 120 °C for 5 h. Different concentrations of PANI (EB form, Alfa Aesar) (1, 2, 5, 10, 15 and 30%) by weight of CdS were prepared (these composites are named as *x*PC where *x* stands for the percentage amount of PANI loaded on CdS). For the synthesis of CdS-PANI composite, required amount of PANI is added in to cadmium chloride solution, sonicated for 10 min and precipitated using Na_2S solution with constant stirring. MoS_2 was synthesized by micromechanical cleavage using the scotch tape technique to yield a few-layered (4–5 layers) MoS_2 flakes [12]. For the synthesis of MoS_2-CdS composite (4% by weight of CdS (4MC)), calculated amount of MoS_2 was added to cadmium chloride solution, sonicated it for 10 min and precipitated using Na_2S solution with constant stirring. For the synthesis of 4M5PC (4% MoS_2 and 5% PANI by weight of CdS) composite, required amount of MoS_2 and PANI were added to aqueous solution of $CdCl_2$, under constant stirring. The solution was sonicated for 10 min continuously. Aqueous solution of Na_2S was added to the above suspension with constant stirring to obtain the MPC composite. All these composites were filtered, washed with water and ethanol followed by heating at 80 °C for 2 h in air.

Pd metal (0.5% by weight) was loaded on 4M5PC (Pd-4M5PC) by a wet impregnation method. Sample powder was kept in contact with aqueous palladium chloride solution and dried under constant stirring followed by heating in an oven at 80 °C for 2 h. To reduce Pd^{2+} to Pd metal, the sample was suspended in Na_2S and Na_2SO_3 solution and irradiated with UV–vis light for 4 h (light source: Xenon arc lamp 300 W). After irradiation, the sample was removed, washed with water and ethanol and dried in oven at 80 °C for 2 h.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns of these samples were recorded using a Philips PW1820 X-ray diffractometer coupled with a PW 1729 generator, which was operated at 30 kV and 20 mA. Graphite crystal monochromator was used for generating monochromatic CuKα radiation. Surface area of the samples was measured using Brunauer, Emmett and Teller (BET) method employing nitrogen as the adsorbing gas. Raman spectra were recorded using 532 nm line from a diode-pumped Nd-YAG laser (power 15 mW) focused to a spot size of about 20 μm. The scattered light was analyzed using a home-built 0.9 m single monochromator coupled with super notch filter and detected by a cooled charge couple device (CCD, Andor technology). The entrance slit was kept at 50 μm, which gave a resolution limited line width of 3 cm^{-1}. Transmission electron microscopy (TEM), high resolution TEM (HRTEM) and selected area electron diffraction (SAED) were carried out using a JEOL, TEM-3010 for microstructural and morphological studies. UV–vis diffused reflectance spectra (UV–vis DRS) of all samples were recorded using a Jasco (model V-670) spectrophotometer equipped with an integrating sphere accessory. Barium sulfate was used as reference for recording the reflectance spectra. Photoluminescence (PL) spectra were recorded with an Edinburgh Instruments FLSP 920 system with a 450 W Xe arc lamp as the excitation source and a red sensitive peltier element cooled Hamamatsu R2658 PMT as the detector. Emission spectra were recorded by exciting the samples at 282 nm. All the emission patterns were corrected for the detector response and were measured at 1 nm resolution. Excited state lifetimes of the charge carriers were measured with the same instrument using a nanosecond Hydrogen flash lamp as the excitation source and a Time Correlated Single Photon Counting (TCSPC) technique. Frequency of the lamp was 40 kHz. The samples were excited at 282 nm and the lifetime was measured for 590 nm emission.

2.3. Photocurrent measurements

For photocurrent measurements, coplanar interdigitated gold electrodes were deposited on CdS, 4MC, 5PC and 4M5PC pellet. These pellets were irradiated using a day light fluorescent lamp (36 W, power density = 1.3 mW cm^{-2}), which consisted of fluorescent emission predominantly in the visible region along with a UV contribution of ~3% under ambient conditions [13]. A bias of 1.0 V was applied to one electrode and the photocurrent produced was measured by Keithley 6517A Electrometer.