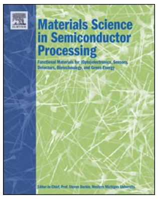
Materials Science in Semiconductor Processing 80 (2018) 44–51

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp



Synthesis and characterization of CdS/MIL-125 (Ti) as a photocatalyst for water splitting

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ARTICLE INFO

Keywords:
MIL-125(Ti)
CdS
Photocatalyst
Artificial photosynthesis

ABSTRACT

Titanium based metal organic framework MIL-125 was incorporated with narrow band-gap semiconductor CdS through a solvothermal approach. Samples with different amounts of CdS loading were prepared and characterized using ICP, N_2-physisorption, PXRD, DRS, SEM, TEM, HRTEM, STEM and EDS methods. The resulting composites were tested for photocatalytic hydrogen production through water splitting with platinum and lactic acid as co-catalyst and sacrificial agent, respectively. The optimized sample (with about 8 wt% CdS) showed 2.8 times higher activity compared to bulk CdS and retained its integrity through both long-term and recycling experiments. As an attempt to further elucidate the mechanism of photocatalytic activity enhancement, CdS/SBA-15 composite was investigated. Both CdS and MIL-125 proved to be active under irradiation but electron injection from CdS to MIL-125 is most likely to be the main mechanism for suppressing charge carrier recombination and also prohibiting photo-corrosion.

1. Introduction

Rapidly increasing global energy demand and serious concerns about the environmental impacts of fossil fuels [1], have left no choice but to develop new technologies for using sustainable energy resources [2]. Solar energy is abundant and free; many efforts have been devoted to find ways of harvesting it, as a result solar cells [3] are widely commercialized today. Meanwhile the best strategy to store solar energy especially for transportation applications is direct conversion by producing energy dance molecules, e.g. H_2 [4]~~.~~; Splitting water using photoactive catalysts is one of the most studied approaches for achieving this goal [5]. Fujushima and Honda were the first to report the ability of TiO_2 to split water under UV irradiation [6]. Since their pioneering publication, many other materials and systems have been investigated [7]; among these, some metal chalcogenides are of especial importance since their electronic levels are in suitable energy positions to reduce water molecules [8] and perform other reactions, e.g. organic dye removal [9]. Cadmium sulfide (CdS) is one of the most important compounds of this class due to its ideal band gap energy (low enough to absorb visible photons, yet enough to perform water splitting) [10]; however some drawbacks limit its widespread use namely, high rate of charge carrier re-combination, lack of proper surface sites for dark reactions involved [11] and instability in reaction conditions due to photo-corrosion [12]. Several strategies have been proposed to improve the activity and robustness of CdS based photocatalysts; including but not limited to surface deposition with co-catalysts e.g. Pt [13], NiS [14], MoS_2 [15], deposition on TiO_2 [16], and incorporation into various porous materials such as Ti-MCM-41 [17].

Metal-organic frameworks (MOFs) have gained widespread attention in the recent years due to some unique properties [18] including high surface area, crystalline and tunable pore structures, their ability for chemical functionalization [19] or loading with different nanoparticles (NPs) [20] through a variety of techniques and approaches. Versatile features of MOFs have made their logical design possible for intended applications including but not limited to~~:~~ semiconductors [21], selective CO_2 capturing [22], hydrogen storage [23], drug delivery [24], catalysts [25] and also photocatalysts for various reactions, namely CO_2 reduction [26], water splitting [27], organic synthesis [28]~~,~~ and pollution degradation [29]. They have also been used for adsorptive removal of organic dyes [30] and even as precursors to obtain other nanomaterials [31]. Loading MOFs with oxide semiconductor NPs (e.g. TiO_2) has also been investigated [32].

In 2013, Wang and co-workers [33] incorporated CdS NPs in chromium based MIL-101 by a post synthetic method and reported a significant enhancement in the photocatalytic activity of resulting composites for hydrogen production under irradiation. Since then the incorporation of CdS in UiO-66 [11,34,35] and MIL-100 [36,37] has been studied for various applications. Other photoactive components

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https://doi.org/10.1016/j.mssp.2018.02.013
Received 7 November 2017; Received in revised form 5 January 2018; Accepted 12 February 2018

such as graphitic-C_3N_4 [38] and Erythosin B [39,40] have been investigated to improve the photocatalytic activity of MOFs.

MIL-125 was first synthesized by Férey and co-workers [41] in 2009 and showed reversible photochromism upon alcohol adsorption. Furthermore, its adsorption properties towards other substances have been investigated [42,43]. Optical response of MIL-125 can be engineered through ligand functionalization [44]. Amine-functionalized NH_2-MIL-125 is able to separate charge carriers under ultraviolet and/or visible irradiation [45]; thus making it suitable for dehydrogenation of formic acid [46], photocatalytic oxidation of amines to imines [47] and visible-light water splitting [48]. Noble metal decorated NH_2-MIL-125 has been studied as a catalyst for ammonia borane hydrolysis [49] also as a photocathode for hydrogen evolution reaction [50]. Yuan and co-workers [51] reported a photodeposition approach to incorporate metal sulfides in MIL-125 and used the resulting materials for photocatalytic reduction of Cr(VI) ions. Liu and co-workers [52] sensitized NH_2-MIL-125 with TiO_2 nanowires to increase water splitting activity. Gascon and co-workers [53] investigated cobaloxime composites of Co@NH2-MIL-125 as hydrogen evolution photocatalysts.

In 2015, Wu and co-workers [54] reported a clean strategy to decorate MIL-125 with noble metal NPs; superior to regular deposition techniques for photocatalytic hydrogen production. In their method, a redox reaction occurs between the titanium containing clusters of photoactivated MIL-125 and the metal salt precursor resulting in small-sized, uniform NPs evenly distributed inside the pores. The ability of MIL-125 to reduce platinum species under irradiation has also been used in the present study.

Herein, we report an in-situ solvothermal deposition of CdS NPs in MIL-125 aimed to improve the hybrid further than each of the single components. Photocatalytic hydrogen evolution activity of the resulting composites were investigated by water splitting with platinum and lactic acid as co-catalyst and sacrificial agent, respectively. The main objective was to prevent photo-corrosion by chemically separating CdS from water molecules while keeping electrical contact through the semiconducting MOF and co-catalyst. In order to study the effectiveness of this approach, long-term and recycling experiments were performed in identical conditions for the optimized sample. The synthesis steps are fairly simple and straightforward, benefiting from several previous studies in the literature and with some modifications, samples were obtained with suitable physicochemical properties known to be necessary for photochemical water splitting [33–35]. Modifications were also applied to the method of photocatalytic activity measurement, both in reactor design (Fig. S1) and to account for weight loss in recycling experiments. Obtained results are comparable with literature values [34].

2. Experimental

2.1. Materials and reagents

All chemicals were of synthetic grade and used without further purification. Terephthalic acid (1,4- banzendicarboxilic acid), cadmium acetate ($Cd(CH_3COO)_2$), chloroplatinic acid (H_2PtCl_6), zinc powder and solvents were purchased from Merck (Germany), Pluronic P123 (PEG-PPG-PEG) was obtained from Sigma-Aldrich (US) and titanium isopropoxide ($C_{12}H_{28}O_4Ti$) from DaeJung® (South Korea). DMF (dimethylformamide $(CH_3)_2NCH$), DMSO (dimethyl sulfoxide $(CH_3)_2SO$), methanol, ethanol and acetone were obtained from Merck.

2.2. Synthesis of MIL-125(Ti)

MIL-125(Ti) was synthesized according to Férey's method [41] with some modifications; 15 mmol of 1,4-banzendicarboxilic acid and 9 mmol of titanium isopropoxide were dissolved in 50 ml of 9:1 dried mixture of DMF: MeOH and transferred to a 200 ml Teflon® lined autoclave which was kept in a pre-heated oven at 150 °C for 16 h. After cooling down to room temperature slowly, the obtained white precipitate was centrifuged and soaked in fresh DMF while being magnetically stirred for 3 days and 2 days in methanol (solvents were both refreshed on a daily basis). After drying at room temperature for one week, the obtained white powder was activated at 200 °C in a static air muffle furnace and stored under argon until further use.

2.3. Growth of CdS nanoparticles on MOF

In-*situ* synthesis of CdS in MIL-125(Ti) was conducted using Wang's method [33] with small modifications; 200 mg of activated MIL-125 was dispersed in 10 ml of DMSO (acting as both as solvent and sulfur source) using ultrasonic bath, then calculated amounts of cadmium acetate were added to the suspension after vigorous magnetic stirring to dissolve the clear crystals of cadmium acetate the mixture was transferred to a Pyrex® 6-dram vial and then placed in a Teflon® lined autoclave, (both were separately sealed with argon) and kept in a pre-heated oven at 180 °C for 12 h. After cooling down to room temperature with the oven, seals were broken under lab hood to avoid the strong sulfur and vinegar fumes. Obtained yellow powders (the saturation of the yellow color depends on the CdS content of each sample) were centrifuged and washed thrice with fresh ethanol and twice with fresh acetone then dried in vacuum at 60 °C for 6 h. Samples were labelled with "**a**-**d**" based on the intended weight content of CdS (**a**: 6%, **b**: 12%, **c**: 24% and **d**: 48%) and stored under argon.

Above mentioned synthesis steps are summarized in Scheme 1.

2.4. Synthesis of control samples

SBA-15 was synthesized according to Zhao's method [55] as an inactive porous replacement for MIL-125 and similarly deposited with 12 wt% of CdS (this loading amount was found to show optimized hydrogen evolution activity in preliminary experiments). Bulk CdS particles were synthesized from a concentrated DMSO solution of cadmium acetate in the same manner mentioned above whiteout any growth limiting agent.

2.5. Characterization and methods

Powder X-Ray diffraction (PXRD) patterns were measured on a Philips (Holland) PW1730 diffractometer with CuK_α ($\lambda = 1.54$ Å) radiation. N_2-physisorption studies were performed on a Micrometrics (US) TriStar II 3020 instrument. Scanning electron micrographs were obtained using a Zeiss (Germany) DSM 960 A instrument working at 30 kV with both SE and BSE signals. Transmission electron micrographs were obtained with a Philips (Holland) CM120 working at 100 kV. HRTEM and STEM studies were performed using a Tecnai F30 microscope (FEI, US) working at 300 kV; transmission electron micrographs were recorded on a coupled CCD camera (Gatan) and High Angle Annular Dark Field (STEM-HAADF) images were obtained with a HAADF detector (Fischione). X-ray Energy Dispersive Spectra (EDS) were obtained with an EDAX detector. Diffuse Reflectance Spectroscopy (DRS) was performed using a Shimadzu (Japan) UV-2550 spectrophotometer with $BaSO_4$ as white standard. Induced Coupled Plasma-Optical emission spectroscopy (ICP-OES) analysis were performed using a Varian (US) VISTA-MPX instrument. FTIR spectra were obtained by KBr pallets using a Nicolet (US) 510 P instrument.

2.6. Photocatalytic measurements

In a typical experiment, 5 mg of photocatalyst (new and control samples) was added to 20 ml of 10 v/v% nitrogen purged solution of lactic acid in double distilled water and transferred to a silicon rubber sealed Pyrex® photoreactor, also 10 µl of H_2PtCl_6 solution (with the Pt content of 2.5 g/l) was added as co-catalyst precursor, the mixture was further purged with nitrogen in darkness and eventually sealed. Our