Solar Hydrogen Generation over CdS Incorporated in Ti-MCM-48

Mesoporous Materials under Visible Light Illumination

Rui Peng^a, Chia-Ming Wu^a, Jonas Baltrusaitis^b, Nada M. Dimitrijevic^c, Tijana Rajh^c, and
Ranjit T. Koodali^{*a}

^a Department of Chemistry, University of South Dakota, Vermillion, South Dakota 57069

^b Department of Chemical Engineering, Lehigh University, Bethlehem, PA 18015

^c Nanoscience and Nanotechnology, and Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439

Fax: 1-605-677-6397; Tel.: 1-605-677-6189; E-mail address: Ranjit.Koodali@usd.edu

Abstract

MCM-48 cubic mesoporous materials containing CdS and spatially isolated titania nanoclusters were prepared in this study. Powder X-ray diffraction (XRD), nitrogen adsorption isotherm, transmission electron microscopy (TEM), atomic absorption spectroscopy (AAS), UV-Visible diffuse reflectance spectroscopy (DRS), X-ray photoelectron spectroscopy (XPS), and electron paramagnetic resonance (EPR) studies were employed for the characterization of the CdS containing Ti-MCM-48 mesoporous materials. In the current study, all the samples showed photocatalytic activity under visible light ($\lambda > 400$ nm) irradiation for production of hydrogen from splitting of water without Pt as a co-catalyst. The solar hydrogen evolution rate by visible light irradiation seemed to be dependent on CdS and TiO₂ content and the most active photocatalyst produced hydrogen at a rate of 2.726 mmol/h/g_{catalyst}. The apparent quantum yield was estimated of this photocatalyst was estimated to be 36.3%.

KEYWORDS: Photocatalysis; Hydrogen evolution; Coupled semiconductor; CdS/TiO₂; MCM-48; Visible light

1. Introduction

Hydrogen, as a highly efficient and carbon neutral energy carrier, is attractive for addressing the energy crisis.. Since the unprecedented work, by Fujishima and Honda in 1972 [1], a wealth of research have been devoted in this field [2, 3, 4, 5, 6, 7]. Among the various semiconductors, titanium dioxide has attracted significant attention [8, 9, 10, 11, 12, 13, 14, 15, 16, 17]. However, owing to the rapid recombination of the charge-carriers, TiO_2 shows modest activity. Hence, in order to promote the efficiency of TiO_2 , charge recombination of the electron-hole pair needs to be minimized.

A commonly employed strategy to minimize charge-carrier recombination is to control the particle size of TiO_2 . In small particle sized semiconductors, the charge-carriers have to traverse a short distance to reach the surface of the photocatalyst and hence, volume recombination of the photogenerated charges can be reduced. Ti^{4+} ions in tetrahedral environment in general exhibit higher activity in comparison to Ti^{4+} ions in octahedral environment. In tetrahedrally coordinated Ti^{4+} ions, ligand-to-metal charge-transfer (LMCT) represented as $[\text{Ti}^{4+}-\text{O}^{2-}] \rightarrow [\text{Ti}^{3+}-\text{O}^-]^*$ occurs on irradiation with light of appropriate energy. In such a process, the electrons are localized on Ti^{3+} and the holes are localized on O^- , and are close to one another. Localization of such electron-hole pairs leads to minimization of electron-hole recombination. The photocatalytic activity of titania incorporated into mesoporous materials have been reported previously [18, 19, 20, 21, 22, 23, 24, 25].

Photocatalysts containing Ti^{4+} ions in tetrahedral environment absorb energy only in the mid-UV range (200-300 nm). Thus, the wide-spread applicability of such photocatalysts is severely constrained. It will be best to design materials that can absorb visible energy so that solar energy can be effectively harnessed. In this respect, CdS has become predominant [26, 27,

28, 29, 30]. CdS based materials have been widely used in photocatalytic reactions [31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41]. However, CdS undergoes photocorrosion. Numerous procedures have been developed to minimize photocorrosion of CdS. For example, attaching CdS to other wide bandgap semiconductors is a common method [42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54]. Another strategy is to incorporate CdS into porous materials [55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66].

In this work, we aim to synergize the two above-mentioned strategies, by preparing MCM-48 containing spatially isolated titania and then embedding CdS in the mesoporous matrix. In such a photocatalyst, on irradiation by visible light, the electrons can travel from the conduction band of CdS to that of TiO₂. However, the valence band of TiO₂ lies at a more positive potential and therefore, the transfer of holes from the valence band of CdS to that of TiO₂ is forbidden. Thus, the charge-carrier recombination is minimized, and the photocatalytic efficiency CdS-Ti-MCM-48 may be enhanced.

MCM-48 mesoporous materials possess large surface area and ordered and regular pores arrayed in a long-range periodicity [67]. We have shown that Ti-MCM-48 mesoporous photocatalysts exhibit significantly enhanced quantum efficiency compared to Ti-MCM-41 [68]. Moreover, we have demonstrated that CdS-MCM-48 show very high photocatalytic hydrogen evolution compared to CdS/ETS-4, CdS/ETS-10, CdS/Zeolite Y, CdS/Zeolite L, CdS/Al-HMS, or CdS-SBA-15 [69].

Previous works regarding CdS and/or TiO₂ incorporated into mesoporous materials suffer from one or more of the following drawbacks: i) lack of a comprehensive and detailed physico-chemical characterization that precludes a clear structure-activity relationship, ii) loading effect of TiO₂ and CdS has not been studied, iii) lack of photocorrosion and recycling studies, iv) lack

of characterization of the chalcogenide semiconductor by XPS, v) use of expensive co-catalyst such as Pt, vi) relatively low quantum yield, and vii) lack of demonstration of electron transfer from CdS to TiO₂. We have previously reported the use of CdS-TiO₂ and RuO₂-CdS-TiO₂ coupled semiconductors as photocatalysts for solar hydrogen evolution, however the yield of hydrogen was found to be modest, *i.e.* 0.92 mmol/h/g_{catalyst} and 0.26 mmol/h/g_{catalyst} [70, 71]. In this work, we have further optimized the preparation method and loading levels and report, a significantly higher solar hydrogen evolution rate of 2.726 mmol/h/g_{catalyst}, a three and ten-fold increase in the production of hydrogen compared to our previous works. Our photocatalysts are effective for hydrogen evolution under visible light irradiation even without Pt.

2. Experimental

2.1 Materials

The surfactant, cetyltrimethylammonium bromide (CTAB, 98%) was purchased from Alfa Aesar. Tetraethyl orthosilicate (TEOS, 98%) was obtained from Acros. Ammonium hydroxide, HPLC grade methanol, cadmium acetate dihydrate, and thiourea were obtained from Fisher Scientific. Ethanol was produced by Pharmo-AAPER. Deionized water was used throughout this study.

2.2 Synthesis

CdS-Ti-MCM-48 mesoporous materials were prepared *via* the following synthetic approach. Ti-MCM-48 was prepared as reported by us previously [72]. Afterwards, CdS was incorporated inside Ti-MCM-48 mesoporous materials by a post-impregnation method.

2.2.1 Synthesis of Ti-MCM-48

1.2 g (3.3 mmol) of cetyltrimethylammonium bromide (CTAB) was added to 50 mL deionized water under vigorous stirring. After it was completely dissolved, 25 mL of ethanol was poured into the clear solution. 6 mL of aqueous NH_3 (0.09 mol) was added to the surfactant solution and then 1.8 mL (8 mmol) of the tetraethyl orthosilicate (TEOS) was added immediately. Finally, a known volume of a stock solution of titanium (IV) isopropoxide dissolved in ethanol was added. After stirring at 300 rpm for 4 h, the powder was recovered by filtration, washed with distilled water, and dried in oven at 80 - 90 °C overnight. The dried powder was then ground finely and calcined at 550 °C for 6 h at a heating rate of 3 °C min⁻¹ to remove the template. The samples with Si/Ti ratios of 200 and 50 in the gel were named Ti-MCM-48-01 and Ti-MCM-48-21, respectively. The final Si/Ti ratios in the final product are reported to be 189 and 47 respectively [72].

2.2.2 Synthesis of CdS-Ti-MCM-48

To 0.15 g of Ti-MCM-48, an appropriate amount of cadmium acetate ($\text{Cd}(\text{OAc})_2$), dissolved in 50 mL of HPLC methanol was added and the suspension was stirred at room temperature for 48 h. Afterwards, thiourea, the sulfur source, dissolved in 25 mL HPLC grade methanol was added to the suspension. The slurry was then refluxed at 70 °C while being stirred for 5 h. The suspension was filtered and washed thoroughly with deionized water and hot methanol. Finally, the wet powder was dried in an oven overnight and this sample is labeled as CdS-Ti-MCM-48. In this work, we synthesized 2 sets of samples with Si/CdS ratios of 50 and 25. These ratios were chosen based on our previous experience in that the hydrogen evolution using CdS-MCM-48 materials were found to be the highest at these ratios in comparison to other Si/CdS ratios of 200 and 100 [69]. At higher amounts of CdS, *i.e.*, Si/CdS ratios of 10, 5 etc., we

observe leaching of CdS from the mesoporous matrix, because of the relatively high loadings of CdS. Thus, we have restricted the Si/CdS ratios based on our previous results and because of leaching observed at higher loadings of CdS (*i.e.* Si/CdS = 10 and 5).

In addition, we have also varied the Si/Ti ratio in the Ti-MCM-48 materials. The ratios of Si/Ti used in this study are 200 and 50 based on two different pre-formed Ti-MCM-48 samples. Again, these two ratios are carefully chosen based on our previous published results. Correspondingly, the four samples are denoted as CdS-Ti-MCM-48-01-25, CdS-Ti-MCM-48-01-50, CdS-Ti-MCM-48-21-25, and CdS-Ti-MCM-48-21-50 where the number 01 and 21 represents Si/Ti ratios of 200 and 50, and the numbers 25 and 50 at the end of the samples denote, the Si/CdS ratios.

2.3 Structural Characterizations

X-ray diffraction (XRD) studies were carried out using a Rigaku Ultima IV instrument. Nitrogen isotherms were obtained using Quantachrome Nova 2200e instrument. The amount of CdS in composite materials was estimated from Atomic Absorption Spectrophotometric (AAS) studies. TEM images were acquired using a JEOL JEM-2100 instrument. The band gaps of the materials were determined using a Cary 100 Bio UV-Vis spectrophotometer equipped with Harrick Scientific diffuse reflectance accessory. The XPS studies were carried out using a Kratos system. Electron paramagnetic resonance (EPR) experiments were performed using a Bruker Elexsys E580 spectrometer. More details regarding the structural characterization are provided in the Electronic Supplementary Information (ESI) section.

2.4 Photocatalytic Hydrogen Evolution

For photocatalytic studies, 40 mg of the mesoporous material was dispersed in 10 mL of deionized water and 10 mL of ethanol in a reactor. The reactor was purged with Ar for 30 min.

and then the photocatalytic reaction was initiated. A Xe lamp (300 W, Newport) was used for irradiation. The lamp housing was furnished with a cutoff filter ($\lambda > 400$ nm) to ensure that visible light was directed onto the mesoporous materials. The suspension was constantly stirred during irradiation. At periodic intervals of time, the head space was analyzed for hydrogen gas using a Gas Chromatograph (SRI 8610C). The apparent quantum yield (AQY) was calculated using the formula,
$$\text{AQY (\%)} = \frac{\text{number of evolved hydrogen molecules} \times 2}{\text{number of incident photons}} \times 100\%.$$

3. Results and Discussion

3.1 Powder XRD Analysis

The presence of cubic mesophase can be inferred from powder XRD studies. Figure 1A presents the XRD patterns for the CdS-Ti-MCM-48 mesoporous materials. The XRD plots of the materials prepared in this study are typical of MCM-48 with $Ia\bar{3}d$ space group. One notices an intense peak around $2\theta = 2.9^\circ$. This peak is due to d_{211} diffraction planes of the cubic MCM-48 phase. In addition, a small shoulder can be seen around $2\theta = 3.4^\circ$, which is due to d_{220} diffraction planes. The distinct shoulder is an indication for the formation of the cubic phase. Powder XRD measurements were also carried out in the high angle regions from $2\theta = 10^\circ$ to 60° in order to check if any bulk TiO_2 or CdS are formed in the mesoporous materials (Figure 1B). All the mesoporous materials show a fairly broad peak between 2θ values of 20 and 30° . This is typical of amorphous silica support. The lack of peaks due to titania and CdS indicate that both of these species are highly dispersed on the mesoporous silica support. This suggests that the titania and the CdS are amorphous in nature and/or present as nanoclusters ($\sim 4\text{-}5$ nm in size). TEM results (discussed later) do indicate the presence of CdS and TiO_2 particles in this size range. In

summary, the powder XRD results indicate the presence of cubic mesophase and that TiO₂ and CdS nanoclusters are highly dispersed on the mesoporous support.

3.2 Textural Properties

The textural properties of the mesoporous materials were investigated. The isotherms are plotted in Figure 2A. The isotherms obtained belong to type IV as per the IUPAC classification. This type of isotherm is typical of periodic mesoporous materials. The isotherms shown in Figure 2A can be explained as follows. At low relative pressures, monolayer adsorption of nitrogen takes place first. Then, multilayer formation takes place. This is followed by capillary condensation. In addition, we notice that between the relative pressure values of P/P_0 of 0.1 and 0.2, there is a steep inflection in comparison to other relative pressure values. The inflection seems similar for all materials examined in the study and this indicates that the pore diameters of the samples are similar. Figure 2B shows the pore size distribution of CdS-Ti-MCM-48 materials. A highly uniform pore size distribution can be perceived. This suggests that incorporation of CdS clusters into Ti-MCM-48 mesoporous materials does not impact the pore size. Table 1 lists the Si/CdS ratios, surface areas, pore volumes, and pore diameters. The surface areas of the mesoporous materials are high and range from 1116 to 1542 m²/g and decrease with increase in loadings of CdS and TiO₂. The pore sizes of the Ti-MCM-48 mesoporous materials prior to loading of CdS nanoclusters are ~ 2.2 nm. After incorporation of CdS, the pore size slightly decreases. Similarly, the pore volume of the Ti-MCM-48 mesoporous materials are relatively higher prior to CdS loading and decreases after encapsulation of CdS indicating that the CdS clusters are mostly confined within the mesopores.

The Si/CdS molar ratios in the final calcined samples were estimated by atomic absorption spectrophotometer (AAS) studies. There is a small change in the Si/CdS molar ratios

between the initial and the final product. This is due to the fact that some of the CdS is removed in the washing step. Interestingly, one notices that the Si/CdS ratios are similar in materials prepared using similar amounts of CdS.

3.3 Transmission Electron Microscopy (TEM)

In order to examine the degree of uniformity of the mesopores in CdS-Ti-MCM-48 materials and the spatial distribution of CdS and TiO₂ species, transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) spectroscopic studies were conducted. Figure 3A shows the TEM image of the material, CdS-Ti-MCM-48-21-25 that exhibited the highest activity. An ordered porous structure can be observed in Figure 3A. TEM analysis confirms the results obtained from powder XRD and N₂ physisorption studies and indicates that the highly ordered 3-D cubic phased mesoporous structure was not impacted by the presence of CdS and TiO₂ semiconductor nanoclusters. Also, the TEM image indicates the presence of dark spots that may be attributed to the presence of CdS and or titania clusters. Figure 3B shows a closer view of the mesoporous materials and two regions shown in red and blue squares are indicated. To understand the relative locations of TiO₂ and CdS species, energy dispersive X-ray spectroscopic (EDX) study was conducted. Figure 3C presents the EDX spectra of the area represented by the blue frame. The strong peaks due to Si and O, which are the main elements of MCM-48, can be found within this area. No peaks due to either CdS or TiO₂ can be detected in the blue rectangle area. In contrast, the EDX spectra of the dark area that is enclosed by the red frame, shown in Figure 3D, exhibit peaks due to Cd, S, and Ti in addition to Si and O atoms. Hence, it can be concluded that the dark regions in the TEM image in Fig. 3A are indeed due to the presence of both CdS and TiO₂, suggesting that these species are present in the CdS-Ti-MCM-48-21-25 sample. The peaks due to Cu and C in both EDX plots are from the carbon coated copper TEM

grids. The 3-D bicontinuous and inter-penetrating network of pores in MCM-48 poses intrinsic challenges in imaging the semiconductor materials dispersed in it. For the purposes of determining the particle sizes of CdS and TiO₂, a series of over-focus and under-focus imaging studies were done. A TEM image obtained from these studies is shown in Fig. 3E. The TEM images indicate that the CdS and TiO₂ particles are in contact with one another. The relative particles sizes of CdS are estimated to be around 3.5-4.0 and 4.0-5.0 nm for TiO₂. UV-Vis DRS studies, which are discussed in the next section also indicate the particles sizes of CdS and TiO₂ to be in this range. Particles with d_{101} spacings of 3.54 and 3.13 Å corresponding to CdS and TiO₂ respectively were discerned in TEM studies.

3.4 UV-Vis Diffuse Reflectance Spectroscopy

Diffuse Reflectance Spectroscopy (DRS) provides important information related to the local environment of Ti⁴⁺ ions and also in estimating the size of CdS. Hence, DRS was employed in this work for the above mentioned purposes. Figure 4 shows the DRS spectra of CdS-Ti-MCM-48 mesoporous materials. Two types of absorption onsets, one in the UV and another in the visible region are seen. These distinct absorption bands are due to the presence of CdS and TiO₂ species, respectively. Incorporation of semiconductor species or clusters in porous materials can constrict their sizes. Hence, due to size quantization effect, a blue shift in the onset of absorption is noticed. Bulk CdS clusters show onset of absorption at wavelengths near 600 nm. The DRS results shown in Figure 4 suggest that all the CdS-Ti-MCM-48 samples show significant blue shift in the absorption onset compared to bulk CdS. In the samples, CdS-Ti-MCM-48-01-50 and CdS-Ti-MCM-48-21-50, in which the CdS contents are similar (Si/CdS = 83 and 80 respectively), the onset of absorption in the visible region is near 510 nm. In the samples, with higher CdS loadings (Si/CdS = 48 and 40 respectively), *i.e.* CdS-Ti-MCM-48-01-

25 and CdS-Ti-MCM-48-21-25, the onset of absorption is slightly shifted to longer wavelengths and appear near 520 nm. Based on the positions of the absorption onset of CdS species in the various samples, the corresponding band gap energies of the CdS species in the mesoporous materials are determined to be in the range of 2.38 to 2.43 eV. In addition, by applying the Brus equation [73], the particle size of the CdS clusters can be calculated to be in a fairly narrow range of 3.5 to 3.8 nm. It can be noticed that the particle sizes of the CdS clusters are larger than the pore diameters (~ 1.9 nm) of the Ti-MCM-48 mesoporous host materials. This phenomenon can be explained by the quantum tunneling effect in which the aggregation of CdS (and TiO_2) clusters takes place in the open and 3-D inter-penetrating network of bi-continuous mesopores of the Ti-MCM-48 support materials and is consistent with our previous reports [57, 69, 70]. Thus, the interpenetrating 3-D network of pores in MCM-48 facilitate the aggregation of CdS nanoclusters leading to CdS particles sizes greater than the pore sizes.

Apart from the absorption band due to CdS species in the visible region, an additional absorption onset can be perceived in UV spectrum due to the presence of TiO_2 . In general, it can be seen that in all the samples that the absorption onset due to TiO_2 , varies from 325 to 340 nm and shows a blue shift compared to that of bulk TiO_2 (380 nm). The band gap of TiO_2 species in CdS-Ti-MCM-48-01 and CdS-Ti-MCM-48-21 samples are determined to be in the range of 3.65 to 3.82 eV. The subtle peak appearing at ~ 215 nm in all the samples indicate a ligand-to-metal charge transfer (LMCT) from oxygen ligands to Ti^{4+} ions in tetrahedral coordination. In addition to the absorption band at ~ 215 nm, a shoulder at ~ 250 nm can be seen in CdS-Ti-MCM-48-01-25 and CdS-Ti-MCM-48-01-50 samples that contain relatively lower amounts of titania ($\text{Si}/\text{Ti} = 189$). This weak shoulder indicates that a small portion of Ti^{4+} ions undergo distortion and are present in either penta- or octahedral coordination. In the CdS-Ti-MCM-48-21-25 and CdS-Ti-

MCM-48-21-50 samples that contain greater amounts of titania ($\text{Si/Ti} = 47$), *i.e.* the shoulder is shifted to ~ 270 nm. This suggests that with an increase of titania content, a larger fraction of Ti^{4+} ions are in octahedral coordination. Since, there are no peaks with absorption near 330 nm, bulk TiO_2 can be ruled out. This is also perhaps one of the reason that the long-range powder XRD results do not show the presence of titania.

3.5 X-ray Photoelectron Spectroscopy (XPS) Studies

X-ray photoelectron spectroscopy (XPS) is a sensitive tool in investigating the surface chemical composition and oxidation state of each component in CdS-Ti-MCM-48 materials. The XPS scan of a representative sample, CdS-Ti-MCM-48-21-25, is shown in Figure 5. Figure 5A shows the O 2p core levels in the CdS-Ti-MCM-48-21-25 sample. A peak centered near 532.7 eV is observed. This is attributed to Si-OH bonds in accordance with our previous report [74]. It has to be noted that the O 1s band observed by us is fairly broad and is thus inclusive of Si-O-Si bonds that appear near 532.3 eV in accordance with our previous observation [74]. Interestingly, no peak due to the presence of Ti-O bond is seen (this typically appears in the range of 529.7 to 530.2 eV from our previous experiences [70, 74, 75]. This may be perhaps due to the relatively low amount of titania and is also consistent with our previous experience. The Cd $3d_{5/2}$ and $3d_{3/2}$ peaks at 404.9 and 411.6 eV that correspond to the Cd^{2+} species are shown in Figure 5B. The difference of binding energy between Cd $3d_{5/2}$ and $3d_{3/2}$ peaks is calculated to be 6.7 ± 0.1 eV. Reference data for the binding energy of Cd $3d_{5/2}$ in CdS is reported to be in the range of 405.1 to 405.4 eV whereas that of Cd $3d_{5/2}$ in CdO is typically in the range of 404.0 to 404.6 eV [76]. We have consistently observed the binding energies of Cd $3d_{5/2}$ and $3d_{3/2}$ peaks to be in the range of 404.7 to 404.9 and 411.6 to 411.7 eV in CdS based photocatalysts [69, 70, 77]. Two S 2p peaks at 161.3 and 162.5 eV in Figure 5C are also observed. Reference data suggest that S $2p_{3/2}$

peak to appear in the range of 161.0 to 162.2, which is similar to the values that we obtained in this work (161.3 eV). Thus, these peaks can be assigned to the S^{2-} species from CdS and the results in this study are similar to our previous work related to CdS-MCM-48 [69]. Therefore, the XPS results suggest that CdS is successfully assembled in the Ti-MCM-48 mesoporous materials.

3.6 Photocatalytic Hydrogen Evolution

The CdS-Ti-MCM-48 samples were evaluated for production of hydrogen under visible light irradiation. Figure 6 shows the photocatalytic hydrogen evolution yields from all of the studied samples. In comparing the photocatalytic activities of the materials with similar titania loadings and varying CdS content, *i.e.* CdS-Ti-MCM-48-01-25 (Si/Ti = 189 and Si/CdS = 48) and CdS-Ti-MCM-48-01-50 (Si/Ti = 189 and Si/CdS = 83), it can be noticed that higher yield of hydrogen is produced in the sample with higher amount of CdS. This trend can be rationalized by the fact that the presence of greater number of CdS clusters in the Ti-MCM-48 mesoporous host can generate a larger number of photoactive sites under the illumination of visible light. Hence, the photocatalytic hydrogen evolution rate of CdS-Ti-MCM-48-01-25 is greater than that of CdS-Ti-MCM-48-01-50. Similarly the photocatalytic activity of CdS-Ti-MCM-48-21-25 is higher than that of CdS-Ti-MCM-48-21-50.

In the samples that contain similar amounts of CdS, for instance, the CdS-Ti-MCM-48-01-25 (Si/CdS = 48) and CdS-Ti-MCM-48-21-25 (Si/CdS = 40) samples, higher solar hydrogen yield is achieved from the sample that contains more TiO_2 . CdS-Ti-MCM-48-21-25 exhibits superior photocatalytic activity to the CdS-Ti-MCM-48-01-25 sample and similarly, the photocatalytic activity of CdS-Ti-MCM-48-21-50 is higher than that of CdS-Ti-MCM-48-01-50. Thus, the photocatalytic activity trend is in the order, CdS-Ti-MCM-48-21-25 > CdS-Ti-MCM-

48-01-25 > CdS-Ti-MCM-48-21-50 > CdS-Ti-MCM-48-01-50. The higher photocatalytic activity in the CdS-Ti-MCM-48-21-25 sample is due to the fact that this sample has greater number of CdS and TiO₂ species dispersed in the mesoporous MCM-48 matrix. The presence of a larger number of TiO₂ and CdS clusters is conducive to a higher chance of intimate contact between CdS and TiO₂. In other words, photoinduced electrons on CdS conduction band have more outlets to escape to the conduction band of TiO₂. As a consequence, the photocatalytic efficiency is enhanced. The photocatalytic hydrogen evolution rate and the corresponding apparent quantum yield (AQY), along with the energy conversion efficiency (ECE) [56], are listed in Table 2.

In addition, a comparison of various CdS encapsulated mesoporous photocatalysts for solar hydrogen evolution is presented in Table 3. It can be seen that the sample CdS-Ti-MCM-48-21-25 exhibits impressive hydrogen evolution rate (2726 $\mu\text{mol/h}$) as well as high apparent quantum yield (36.3%) among all reported CdS based periodic mesoporous photocatalytic systems. The high activity of the CdS-Ti-MCM-48 system in comparison to other previous photocatalysts is the presence of highly dispersed CdS with small particle sizes and spatially isolated titania dispersed in a highly open, interconnected, and porous silica support. Such a carefully designed photocatalyst allows for effective transport of electrons from CdS to titania upon visible light irradiation. The relatively small particles of CdS minimizes charge-carrier recombination in the bulk and the presence of tetrahedrally coordinated titania minimizes back electron transfer to CdS. In addition, as indicated by us previously [70], the holes in the valence band may be trapped in the siliceous pore walls, thereby, minimizing recombination of electrons and holes in CdS. Also, the cubic silica support provides a robust and mechanical support for the dispersion of CdS and TiO₂, and by shielding their direct contact with the electrolyte,

photocorrosion of CdS is minimized significantly. Thus, due to the above mentioned synergistic factors, relatively high apparent quantum yield is observed in our system and is higher than the cumulative effects of dispersing CdS and titania in MCM-48.

3.7 Electron Paramagnetic Resonance (EPR) Analysis

In order to elucidate the photoinduced charge carriers transfer pathways in CdS-Ti-MCM-48 samples, electron paramagnetic resonance (EPR) studies were carried out. Irradiation of CdS by visible light leads to the production of electron-hole pairs. Electrons promoted to conduction band in CdS by visible light irradiation can be injected into TiO_2 . EPR signals were monitored by irradiating the sample with visible light (cut off filter 400 nm) in the presence of glycerol. Figure 7 depicts the EPR spectrum of CdS-Ti-MCM-48-21-25 sample. The EPR spectrum of CdS-Ti-MCM-48-21-25 indicates the formation of Ti^{3+} ($g_{\perp} = 1.958$ and $g_{\parallel} = 1.920$) that is evidence for electron transfer from CdS to TiO_2 . A strong signal near $g = 2.004$ is due to organic radicals formed by the reaction of photogenerated holes with glycerol. Thus, the EPR results unambiguously prove the injection of electrons from CdS clusters to titania in the MCM-48 matrix.

3.8 Recycling Studies

The stability of the photocatalysts were evaluated by reusing the materials. Figure 8 shows the photocatalytic hydrogen yield of CdS-Ti-MCM-48-21-25 sample after irradiation for 18 h and the corresponding values are also listed in Table 4. The amount of hydrogen evolved is nearly constant after prolonged irradiation. In our study, we have not added any sulfide and/or sulfite ions as sacrificial reagents nor have we used Pt as a co-catalyst and thus our results are very interesting. In our previous work, with CdS-MCM-48 mesoporous photocatalysts, a 30% loss in photocatalytic activity was observed after one cycle under identical experimental

conditions [69]. However, in this study, we observe highly reproducible hydrogen evolution yields in CdS-Ti-MCM-48-21-25. Thus, by coupling CdS with spatially isolated and well-dispersed titania in MCM-48, one can realize enhanced photocatalytic activity as well as improve the stability of CdS significantly.

The recycled photocatalysts were examined by a variety of methods. The low angle XRD patterns of CdS-Ti-MCM-48-21-25 sample and the corresponding spent sample are shown in Figure 9A. The powder XRD plots are similar and thus the cubic MCM-48 phase is not destroyed upon irradiation. Figure 9B shows the wide angle XRD plot. A broad peak due to amorphous silica is seen. These suggest that MCM-48 is a robust support for dispersing CdS and titania clusters.

We were also interested in knowing if there were any differences in the textural properties of the fresh and the spent catalyst. Figure 10A shows the isotherms of the fresh and spent CdS-Ti-MCM-48-21-25 samples. The isotherms are similar in nature and like-wise the pore size distribution plots (Figure 10B) are also similar indicating that the pores sizes are nearly the same as indicated in Table 5. AAS study of the spent catalyst suggests a small loss of CdS (< 10%) after the photocatalytic reaction. Furthermore, XPS analysis of the spent CdS-Ti-MCM-48-21-25 catalyst was carried out to elucidate the robustness of the photocatalyst under our experimental conditions. Figure 11 presents the XPS spectra of the O, Cd, and S components in the spent CdS-Ti-MCM-48-21-25 sample. As can be seen in Figure 11A, O 2p core levels in the CdS-Ti-MCM-48-21-25 spent catalyst indicates a peak at binding energy of 532.7 eV that can be assigned to the presence of Si-OH bond. However, unlike the O 2p spectra of the fresh CdS-Ti-MCM-48-21-25 sample (shown in Figure 5A), apart from a strong O 2p signal from Si-O-Si moieties, a relatively less intense peak can also be perceived at a binding energy of ~ 530 eV.

This band can be accredited to the presence of Ti-O bond that originates from the TiO₂ nanoclusters in the Ti-MCM-48 support materials. During the photocatalytic processes, a small amount of TiO₂ nanoclusters embedded in the mesopore matrix may be partly exposed due to the detachment of some CdS particles. This explains the presence of bands due to Ti-O bonds in the XPS of the spent catalyst. Despite the subtle detachment of CdS from the TiO₂ sites, the catalyst remains fairly stable and resistant to photocorrosion even after a relative long period of irradiation of visible light. As can be observed in Figure 11B, the XPS of the spent catalysts indicate Cd 3d_{5/2} and 3d_{3/2} peaks at identical binding energies of 404.9 and 411.6 eV as seen in the fresh sample (Figure 5B). More importantly, in Figure 11C, the two S 2p peaks are observed at 161.3 and 162.5 eV indicating the presence and retention of CdS in the mesopore matrix. Fig. S1 shows the TEM image of the spent CdS-Ti-MCM-48-21-25 photocatalyst. One can see the particles of CdS and TiO₂ even in the spent catalyst. The Si/CdS ratio in the spent catalyst is about 10% lower than in the fresh catalyst suggesting some loss of loosely bound CdS from the mesopores during the photocatalytic reaction. Indeed, AAS analysis of the supernatant solution (after photocatalytic reaction and centrifugation) indicate the presence of Cd²⁺ indicating very modest loss of CdS (~ 10%) from the MCM-48 matrix. This result is interesting since we do not observe the formation of CdO after prolonged photocatalytic reaction. In CdS encapsulated in zeolites, CdO has been observed after irradiation [57]. Therefore, the spent catalysts maintain almost identical photocatalytic activities compared to the fresh ones. The physisorption studies are in good agreement with powder XRD analyses. The periodicity of the mesoporous structures in the photocatalysts are not destroyed during the photocatalytic processes and that both CdS and TiO₂ are well dispersed in the host mesoporous materials. A summary of the textural properties of the CdS-Ti-MCM-48-21-25 fresh and spent catalysts are shown in Table 5.

4. Conclusions

CdS-Ti-MCM-48 cubic phased mesoporous were prepared by a post-impregnation method. CdS and TiO₂ species can be well dispersed in the MCM-48 mesoporous materials since no peaks due to bulk CdS or TiO₂ were found. Low angle XRD, TEM, and nitrogen physisorption studies indicate that the ordered cubic phase of Ti-MCM-48 was preserved after the introduction of CdS. All the studied samples showed photocatalytic hydrogen evolution under visible light irradiation even without of Pt as a co-catalyst for H₂ production and sulfide/sulfite as sacrificial agents. This study indicates that CdS-Ti-MCM-48-21-25 exhibits high efficiency; the apparent quantum yield of this material was found to be 36.3% without any co-catalyst. In addition, the recycling study suggested that the stability of CdS in the CdS-Ti-MCM-48 samples was significantly enhanced and the loss of CdS after prolonged period of irradiation was determined to be less than 10%.

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References

- [1] Fujishima A, Honda K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature*. 1972;238:37-8.
- [2] AshokKumar M. An Overview on Semiconductor Particulate Systems for Photoproduction of Hydrogen. *Int J Hydrogen Energy*,. 1998;23:427-38.
- [3] Kudo A, Miseki Y. Heterogeneous photocatalyst materials for water splitting-Rev. *Chemical Society Reviews*. 2009;38:253-78.
- [4] Chen X, Shen S, Guo L, Mao SS. Semiconductor-based Photocatalytic Hydrogen Generation. *Chemical Reviews*. 2010;110:6503-70.

- [5] Takata T, Tanaka A, Hara M, Kondo JN, Domen K. Recent progress of photocatalysts for overall water splitting. *Catalysis Today*. 1998;44:17-26.
- [6] Osterloh FE. Inorganic Materials as Catalysts for Photochemical Splitting of Water. *Chemistry of Materials*. 2007;20:35-54.
- [7] Maeda K. Photocatalytic water splitting using semiconductor particles: History and recent developments. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*. 2011;12:237-68.
- [8] Chae J-H, Lee J-H, Jeong J-H, Kang M-S. Hydrogen Production from Photo Splitting of Water Using the Ga-incorporated TiO₂s Prepared by a Solvothermal Method and Their Characteristics. *Bulletin of the Korean Chemical Society*. 2009;30:302-8.
- [9] Lalitha K, Reddy JK, Phanikrishna Sharma MV, Kumari VD, Subrahmanyam M. Continuous hydrogen production activity over finely dispersed Ag₂O/TiO₂ catalysts from methanol:water mixtures under solar irradiation: A structure-activity correlation. *International Journal of Hydrogen Energy*. 2010;35:3991-4001.
- [10] Moon S-C, Mametsuka H, Tabata S, Suzuki E. Photocatalytic production of hydrogen from water using TiO₂ and B/TiO₂. *Catalysis Today*. 2000;58:125-32.
- [11] Ni M, Leung MKH, Leung DY, Sumathy K. A review and recent developments in photocatalytic water-splitting using TiO₂ for hydrogen production. *Renewable and Sustainable Energy Reviews*. 2007;11:401-25.
- [12] Park J-W, Kang M. Synthesis and characterization of Ag_xO, and hydrogen production from methanol photodecomposition over the mixture of Ag_xO and TiO₂. *International Journal of Hydrogen Energy*. 2007;32:4840-6.
- [13] Park M-S, Kang M. The preparation of the anatase and rutile forms of Ag-TiO₂ and hydrogen production from methanol/water decomposition. *Materials Letters*. 2008;62:183-7.
- [14] Xu S, Ng J, Zhang X, Bai H, Sun DD. Fabrication and comparison of highly efficient Cu incorporated TiO₂ photocatalyst for hydrogen generation from water. *International Journal of Hydrogen Energy*. 2010;35:5254-61.
- [15] Xu S, Sun DD. Significant improvement of photocatalytic hydrogen generation rate over TiO₂ with deposited CuO. *International Journal of Hydrogen Energy*. 2009;34:6096-104.
- [16] Sasikala R, Sudarsan V, Sudakar C, Naik R, Sakuntala T, Bharadwaj SR. Enhanced photocatalytic hydrogen evolution over nanometer sized Sn and Eu doped titanium oxide. *International Journal of Hydrogen Energy*. 2008;33:4966-73.
- [17] Zalas M, Laniecki M. Photocatalytic hydrogen generation over lanthanides-doped titania. *Solar Energy Materials and Solar Cells*. 2005;89:287-96.
- [18] Anpo M, Kim T-H, Matsuoka M. The design of Ti-, V-, Cr-oxide single-site catalysts within zeolite frameworks and their photocatalytic reactivity for the decomposition of undesirable molecules--The role of their excited states and reaction mechanisms. *Catalysis Today*. 2009;142:114-24.
- [19] Anpo M, Yamashita H, Ikeue K, Fujii Y, Zhang SG, Ichihashi Y, et al. Photocatalytic reduction of CO₂ with H₂O on Ti-MCM-41 and Ti-MCM-48 mesoporous zeolite catalysts. *Catalysis Today*. 1998;44:327-32.
- [20] Hu Y, Wada N, Tsujimaru K, Anpo M. Photo-assisted synthesis of V and Ti-containing MCM-41 under UV light irradiation and their reactivity for the photooxidation of propane. *Catalysis Today*. 2007;120:139-44.
- [21] Chien S, Huang K, Kuo M. Photocatalytic decomposition of nitric oxide on TiO₂ modified MCM-41 catalysts. In: E. van Steen MC, Callanan LH, editors. *Studies in Surface Science and Catalysis*: Elsevier; 2004. p. 2876-83.
- [22] Hu Y, Higashimoto S, Martra G, Zhang J, Matsuoka M, Coluccia S, et al. Local Structures of Active Sites on Ti-MCM-41 and Their Photocatalytic Reactivity for the Decomposition of NO. *Catalysis Letters*. 2003;90:161-3.
- [23] Hu Y, Martra G, Zhang J, Higashimoto S, Coluccia S, Anpo M. Characterization of the Local Structures of Ti-MCM-41 and Their Photocatalytic Reactivity for the Decomposition of NO into N₂ and O₂. *The Journal of Physical Chemistry B*. 2006;110:1680-5.

- [24] Ikeue K, Nozaki S, Ogawa M, Anpo M. Photocatalytic Reduction of CO₂ with H₂O on Ti-Containing Porous Silica Thin Film Photocatalysts. *Catalysis Letters*. 2002;80:111-4.
- [25] Hwang JS, Chang JS, Park SE, Ikeue K, Anpo M. High performance photocatalytic reduction of CO₂ with H₂O by Ti-SBA-15 mesoporous material. In: Sang-Eon Park J-SC, Kyu-Wan L, editors. *Studies in Surface Science and Catalysis*; Elsevier; 2004. p. 299-302.
- [26] Shangguan W, Yoshida A. Photocatalytic Hydrogen Evolution from Water on Nanocomposites Incorporating Cadmium Sulfide into the Interlayer. *The Journal of Physical Chemistry B*. 2002;106:12227-30.
- [27] Koca A, Sahin M. Photocatalytic hydrogen production by direct sun light from sulfide/sulfite solution. *International Journal of Hydrogen Energy*. 2002;27:363-7.
- [28] Milczarek G, Kasuya A, Mamykin S, Arai T, Shinoda K, Tohji K. Optimization of a two-compartment photoelectrochemical cell for solar hydrogen production. *International Journal of Hydrogen Energy*. 2003;28:919-26.
- [29] Mrowetz M, Balcerski W, Colussi AJ, Hoffmann MR. Oxidative Power of Nitrogen-Doped TiO₂ Photocatalysts under Visible Illumination. *The Journal of Physical Chemistry B*. 2004;108:17269-73.
- [30] Ranjit KT, Krishnamoorthy R, Varadarajan TK, Viswanathan B. Photocatalytic reduction of nitrite on CdS. *J Photochem Photobiol A: Chem*. 1995;86:185-9.
- [31] Kumar A, Kumar S. Catalytic effect of Ag⁺ in colloidal CdS-induced photooxidation of aniline. *Chemistry Letters*. 1996:711-2.
- [32] Kumar A, Jain AK. Photophysics and photocatalytic properties of Ag⁺-activated sandwich Q-CdS-TiO₂. *Journal of Photochemistry and Photobiology a-Chemistry*. 2003;156:207-18.
- [33] Cong RM, Luo YJ, Yu HQ. Effect of Polymer Templates on the Preparation and Photocatalytic Activity of CdS Quantum Dots. *Acta Chimica Sinica*. 2010;68:1971-6.
- [34] Ghows N, Entezari MH. Exceptional catalytic efficiency in mineralization of the reactive textile azo dye (RB5) by a combination of ultrasound and core-shell nanoparticles (CdS/TiO₂). *Journal of Hazardous Materials*. 2011;195:132-8.
- [35] Kirovskaya IA, Timoshenko OT, Karpova EO. The catalytic and photocatalytic properties of InP-CdS and ZnTe-CdS system components. *Russian Journal of Physical Chemistry A*. 2011;85:557-60.
- [36] Nayak J, Lohani H, Bera TK. Observation of catalytic properties of CdS-ZnO composite nanorods synthesized by aqueous chemical growth technique. *Current Applied Physics*. 2011;11:93-7.
- [37] Maji SK, Dutta AK, Dutta S, Srivastava DN, Paul P, Mondal A, et al. Single-source precursor approach for the preparation of CdS nanoparticles and their photocatalytic and intrinsic peroxidase like activity. *Applied Catalysis B-Environmental*. 2012;126:265-74.
- [38] Shinde MD, Chavan PG, Umarji GG, Arbuj SS, Rane SB, More MA, et al. Field Emission and Photo-Catalytic Investigations on Hierarchical Nanostructures of Copper Doped CdS Synthesized by Kitchen-Chemistry Approach. *Journal of Nanoscience and Nanotechnology*. 2012;12:3788-98.
- [39] Chen XF, Zhang J, Huo YN, Li HX. Preparation and visible light catalytic activity of three-dimensional ordered macroporous CdS/TiO₂ films. *Chinese Journal of Catalysis*. 2013;34:949-55.
- [40] Zhu L, Meng ZD, Park CY, Ghosh T, Oh WC. Characterization and relative sonocatalytic efficiencies of a new MWCNT and CdS modified TiO₂ catalysts and their application in the sonocatalytic degradation of rhodamine B. *Ultrasonics Sonochemistry*. 2013;20:478-84.
- [41] Jana TK, Pal A, Chatterjee K. Self assembled flower like CdS-ZnO nanocomposite and its photo catalytic activity. *Journal of Alloys and Compounds*. 2014;583:510-5.
- [42] Li G-S, Zhang D-Q, Yu JC. A New Visible-Light Photocatalyst: CdS Quantum Dots Embedded Mesoporous TiO₂. *Environmental Science & Technology*. 2009;43:7079-85.
- [43] Fujii H, Ohtaki M, Eguchi K, Arai H. Preparation and photocatalytic activities of a semiconductor composite of CdS embedded in a TiO₂ gel as a stable oxide semiconducting matrix. *Journal of Molecular Catalysis A: Chemical*. 1998;129:61-8.
- [44] Wang X, Liu G, Chen Z-G, Li F, Wang L, Lu GQ, et al. Enhanced photocatalytic hydrogen evolution by prolonging the lifetime of carriers in ZnO/CdS heterostructures. *Chemical Communications*. 2009:3452-4.

- [45] Biswas S, Hossain MF, Takahashi T, Kubota Y, Fujishima A. Comparative study of photocatalytic activity in CdS–TiO₂ thin films prepared by two different techniques. *Journal of Vacuum Science & Technology: Part A*. 2008;26:1002-6.
- [46] Biswas S, Hossain MF, Takahashi T, Kubota Y, Fujishima A. Photocatalytic activity of high-vacuum annealed CdS–TiO₂ thin film. *Thin Solid Films*. 2008;516:7313-7.
- [47] Chen Y, Wang L, Lu G, Yao X, Guo L. Nanoparticles enwrapped with nanotubes: A unique architecture of CdS/titanate nanotubes for efficient photocatalytic hydrogen production from water. *Journal of Materials Chemistry*. 2011;21.
- [48] Jang JS, Choi SH, Kim HG, Lee JS. Location and State of Pt in Platinized CdS/TiO₂ Photocatalysts for Hydrogen Production from Water under Visible Light. *The Journal of Physical Chemistry C*. 2008;112:17200-5.
- [49] Kida T, Guan G, Minami Y, Ma T, Yoshida A. Photocatalytic hydrogen production from water over a LaMnO₃/CdS nanocomposite prepared by the reverse micelle method. *Journal of Materials Chemistry*. 2003;13:1186-91.
- [50] Park H, Choi W, Hoffmann MR. Effects of the preparation method of the ternary CdS/TiO₂/Pt hybrid photocatalysts on visible light-induced hydrogen production. *Journal of Materials Chemistry*. 2008;18:2379-85.
- [51] So WW, Kim KJ, Moon SJ. Photo-production of hydrogen over the CdS-TiO₂ nano-composite particulate films treated with TiCl₄. *International Journal of Hydrogen Energy*. 2004;29:229-34.
- [52] Wang X, Liu G, Chen Z-G, Li F, Lu GQ, Cheng H-M. Efficient and stable photocatalytic H₂ evolution from water splitting by (Cd_{0.8}Zn_{0.2})S nanorods. *Electrochemistry Communications*. 2009;11:1174-8.
- [53] Yan H, Yang J, Ma G, Wu G, Zong X, Lei Z, et al. Visible-light-driven hydrogen production with extremely high quantum efficiency on Pt–PdS/CdS photocatalyst. *Journal of Catalysis*. 2009;266:165-8.
- [54] Zhu J, Yang D, Geng J, Chen D, Jiang Z. Synthesis and characterization of bamboo-like CdS/TiO₂ nanotubes composites with enhanced visible-light photocatalytic activity. *Journal of Nanoparticle Research*. 2008;10:729-36.
- [55] Guan G, Kida T, Kusakabe K, Kimura K, Abe E, Yoshida A. Photocatalytic activity of CdS nanoparticles incorporated in titanium silicate molecular sieves of ETS-4 and ETS-10. *Applied Catalysis A: General*. 2005;295:71-8.
- [56] Guan G, Kida T, Kusakabe K, Kimura K, Fang X, Ma T, et al. Photocatalytic H₂ evolution under visible light irradiation on CdS/ETS-4 composite. *Chemical Physics Letters*. 2004;385:319-22.
- [57] Ryu SY, Balcerski W, Lee TK, Hoffmann MR. Photocatalytic Production of Hydrogen from Water with Visible Light Using Hybrid Catalysts of CdS Attached to Microporous and Mesoporous Silicas. *The Journal of Physical Chemistry C*. 2007;111:18195-203.
- [58] Fox MA, Pettit TL. Photoactivity of zeolite-supported cadmium sulfide: hydrogen evolution in the presence of sacrificial donors. *Langmuir*. 1989;5:1056-61.
- [59] Hirai T, Bando Y. Immobilization of CdS nanoparticles formed in reverse micelles onto aluminosilicate supports and their photocatalytic properties. *Journal of Colloid and Interface Science*. 2005;288:513-6.
- [60] Hirai T, Ota M. Immobilization of CdS nanoparticles from reverse micellar system onto mesoporous organosilicates and their photocatalytic properties. *Materials Research Bulletin*. 2006;41:19-28.
- [61] Zhang YJ, Zhang L, Li S. Synthesis of Al-substituted mesoporous silica coupled with CdS nanoparticles for photocatalytic generation of hydrogen. *International Journal of Hydrogen Energy*. 2010;35:438-44.
- [62] Zhang YJ, Zhang L. Preparation of Ru-loaded CdS/Al-HMS nanocomposites and production of hydrogen by photocatalytic degradation of formic acid. *Applied Surface Science*. 2009;255:4863-6.
- [63] Jing D, Guo L. Efficient Hydrogen Production by a Composite CdS/Mesoporous Zirconium Titanium Phosphate Photocatalyst under Visible Light. *The Journal of Physical Chemistry C*. 2007;111:13437-41.

- [64] Shen S, Guo L. Growth of quantum-confined CdS nanoparticles inside Ti-MCM-41 as a visible light photocatalyst. *Materials Research Bulletin*. 2008;43:437-46.
- [65] Lunawat P, Kumar R, Gupta N. Structure Sensitivity of Nano-structured CdS/SBA-15 Containing Au and Pt Co-catalysts for the Photocatalytic Splitting of Water. *Catalysis Letters*. 2008;121:226-33.
- [66] Hirai T, Nanba M, Komasa I. Dithiol-mediated incorporation of CdS nanoparticles from reverse micellar system into Zn-doped SBA-15 mesoporous silica and their photocatalytic properties. *Journal of Colloid and Interface Science*. 2003;268:394-9.
- [67] Zhao D, Wan Y. On the Controllable Soft-Templating Approach to Mesoporous Silicates-Rev. *Chemical Reviews*. 2007;107:2821-60.
- [68] Peng R, Zhao D, Dimitrijevic NM, Rajh T, Koodali RT. Room Temperature Synthesis of Ti-MCM-48 and Ti-MCM-41 Mesoporous Materials and Their Performance on Photocatalytic Splitting of Water. *Journal of Physical Chemistry: C*. 2012;116:1605-13.
- [69] Peng R, Zhao D, Baltrusaitis J, Wu C-M, Koodali RT. Visible light driven photocatalytic evolution of hydrogen from water over CdS encapsulated MCM-48 materials. *RSC Advances*. 2012;2:5754-67.
- [70] Peng R, Lin C, Baltrusaitis J, Wu C-M, Dimitrijevic NM, Rajh T, et al. Insight into band positions and inter-particle electron transfer dynamics between CdS nanoclusters and spatially isolated TiO₂ dispersed in cubic MCM-48 mesoporous materials: a highly efficient system for photocatalytic hydrogen evolution under visible light illumination. *Phys Chem Chem Phys*. 2014;16:2048-61.
- [71] Peng R, Wu CM, Baltrusaitis J, Dimitrijevic NM, Rajh T, Koodali RT. Ultra-stable CdS incorporated Ti-MCM-48 mesoporous materials for efficient photocatalytic decomposition of water under visible light illumination. *Chemical Communications*. 2013;49:3221-3.
- [72] Zhao D, Budhi S, Rodriguez A, Koodali RT. Rapid and facile synthesis of Ti-MCM-48 mesoporous material and the photocatalytic performance for hydrogen evolution. *International Journal of Hydrogen Energy*. 2010;35:5276-83.
- [73] Steigerwald ML, Brus LE. Synthesis, Stabilization, and Electronic Structure of Quantum Semiconductor Nanoclusters. *Annual Review of Materials Science*. 1989;19:471-95.
- [74] Rasalingam S, Kibombo HS, Wu CM, Budhi S, Peng R, Baltrusaitis J, et al. Influence of Ti-O-Si hetero-linkages in the photocatalytic degradation of Rhodamine B. *Catalysis Communications*. 2013;31:66-70.
- [75] Peng R, Baltrusaitis J, Wu CM, Koodali RT. Pd-Ti-MCM-48 cubic mesoporous materials for solar simulated hydrogen evolution. *International Journal of Hydrogen Energy*. 2015;40:905-18.
- [76] NIST X-ray Photoelectron Spectroscopy Database, Version 41 (National Institute of Standards and Technology, Gaithersburg, 2012); <http://srdata.nist.gov/xps/>.
- [77] Parayil SK, Baltrusaitis J, Wu CM, Koodali RT. Synthesis and characterization of ligand stabilized CdS-Trititanate composite materials for visible light-induced photocatalytic water splitting. *International Journal of Hydrogen Energy*. 2013;38:2656-69.

Solar Hydrogen Generation over CdS Incorporated Ti-MCM-48 Mesoporous Materials under Visible Light Illumination

Rui Peng, Chia-Ming Wu, Jonas Baltrusaitis,

Nada M. Dimitrijevic, Tijana Rajh, and Ranjit T. Koodali*

Figure Captions

Figure 1. (A) Low-angle XRD patterns of all studied CdS-Ti-MCM-48 samples and (B) High-angle XRD patterns of all studied CdS-Ti-MCM-48 samples.

Figure 2. (A) Nitrogen physisorption isotherms of all studied CdS-Ti-MCM-48 samples; and (B) Pore size distribution plots of all studied CdS-Ti-MCM-48 samples.

Figure 3. (A) and (B) TEM image of CdS-Ti-MCM-48-21-25; (C) EDX plot of blue frame area indicated in (B); (D) EDX plot of red frame area in (B) and (E) showing d spacing of CdS and TiO₂ particles.

Figure 4. Diffuse reflectance spectra of studied CdS-Ti-MCM-48 samples.

Figure 5. (A) XPS of O peaks from CdS-Ti-MCM-48-21-25 sample; (B) XPS of Cd peaks from CdS-Ti-MCM-48-21-25 sample; and (C) XPS of S peaks from CdS-Ti-MCM-48-21-25 sample.

Figure 6. Photocatalytic hydrogen yields of studied CdS-Ti-MCM-48 samples.

Figure 7. EPR spectra of CdS-Ti-MCM-48-21-25 sample. A strong signal near $g = 2.004$ is due to organic radicals formed by the reaction of photogenerated holes with glycerol.

Figure 8. Photocatalytic hydrogen evolution over CdS-Ti-MCM-48-21-25 and its spent catalyst.

Figure 9. (A) Low angle XRD patterns of fresh and spent CdS-Ti-MCM-48-21-25 samples; and (B) High angle XRD patterns of fresh and spent CdS-Ti-MCM-48-21-25 samples.

Figure 10. (A) Nitrogen physisorption isotherms of fresh and spent CdS-Ti-MCM-48-21-25 samples; and (B) Pore size distribution plots of fresh and spent CdS-Ti-MCM-48-21-25 samples.

Figure 11. (A) XPS of O peaks from CdS-Ti-MCM-48-21-25-spent sample; (B) XPS of Cd peaks from CdS-Ti-MCM-48-21-25-spent sample; and (C) XPS of S peaks from CdS-Ti-MCM-48-21-25-spent sample.

Figure 1

Figure 1B

Figure 2A

Figure 2B

Figure 3

Figure 4

Figure 5A

Figure 5B

Figure 5C

Figure 6

Figure 7

Figure 8

Figure 9A

Figure 9B

Figure 10A

Figure 10B

Figure 11A

Figure 11B

Figure 11C

Table 1. Textural properties of all studied CdS-Ti-MCM-48 samples.

Material	Si/CdS ^a (mol)	Si/CdS ^b (mol)	Surface Area ^c $\text{m}^2 \text{g}^{-1}$	Pore Volume ^d $\text{cm}^3 \text{g}^{-1}$	Pore Diameter ^e (Å)
CdS-Ti-MCM-48-01-25	25	48	1542	0.81	19.5
CdS-Ti-MCM-48-01-50	50	83	1464	0.96	19.4
CdS-Ti-MCM-48-21-25	25	40	1139	0.66	19.3
CdS-Ti-MCM-48-21-50	50	80	1116	0.67	19.4

^a Molar ratio in the synthesis gel

^b Molar ratio in the product measured by AAS study

^c Determined by applying the Brunauer-Emmett-Teller (BET) equation to a relative pressure (P/P_0) range of 0.05–0.30 to the adsorption isotherm

^d Calculated from the amount of nitrogen adsorbed at the highest relative pressure (P/P_0) ~ 0.98

^e Calculated from the Barrett-Joyner-Halenda (BJH) equation using the desorption isotherm

Table 2. Summary of photocatalytic hydrogen evolution rate and apparent quantum yield (AQY) of the studied samples.

Material	Hydrogen evolution rate (mmol/h/g _{catalyst})	AQY	ECE
CdS-Ti-MCM-48-01-50	0.275	3.7%	3.5%
CdS-Ti-MCM-48-01-25	1.251	16.7%	15.9%
CdS-Ti-MCM-48-21-50	0.899	12.0%	11.4%
CdS-Ti-MCM-48-21-25	2.726	36.3%	34.7%

$$\text{AQY (\%)} = \frac{\text{the number of evolved H}_2 \text{ molecules} \times 2}{\text{the number of incident photons}} \times 100\%$$

$$\text{ECE (\%)} = \frac{\text{combustion enthalpy of evolved H}_2}{\text{energy of incident photons}} \times 100\%$$

Table 3. Comparison of solar hydrogen evolution over CdS supported on various periodic mesoporous materials.

Catalyst	Experimental condition	Hydrogen evolution rate ($\mu\text{mol/h}$)	Ref.
CdS/SBA-15	0.2 g catalyst + 50 mL of 50:50 ethanol/water, 500 W Hg-Xe arc lamp, $\lambda > 400$ nm.	2.7 (AQY: NA)	[81]
CdS/SBA-15	0.1 g catalyst + 20 mL of water + 15 vol.% 2-propanol, 500 W Halogen lamp.	133.3 (AQY: NA)	[85]
Pt/CdS/SBA-15	0.1 g catalyst + 20 mL of water + 15 vol.% 2-propanol, 500 W Halogen lamp.	800 (AQY: NA)	[85]
CdS-ZnSBA-15	0.02 g catalyst + 20 mL of water + 15 vol.% 2-propanol, 2000 W Xe lamp, $\lambda > 400$ nm.	0.703 (AQY: NA)	[87]
CdS/Al-HMS	0.2 g catalyst + 200 mL of aqueous formic acid solution ($\text{H}_2\text{O} : \text{HCOOH} = 4:1$, in volume), 350 W Xe lamp, $\lambda > 420$ nm.	23.7 (AQY=1.2%)	[90]
Ru/CdS/Al-HMS	0.2 g catalyst + 200 mL of aqueous formic acid solution ($\text{H}_2\text{O} : \text{HCOOH} = 4:1$, in volume), 350 W Xe lamp, $\lambda > 420$ nm.	590 (AQY=5.92%)	[90]
CdS@Ti-MCM-41	0.2 g catalyst + Na_2SO_3 (0.38 M, 200 mL) solution, 350 W Xe lamp, $\lambda > 430$ nm.	250 (AQY=0.74%)	[93]
Pt/CdS@Ti-MCM-41	0.2 g catalyst + Na_2SO_3 (0.38 M, 200 mL) solution, 350 W Xe lamp, $\lambda > 430$ nm.	875 (AQY=2.6%)	[93]
CdS-MCM-48-25	0.04 g catalyst + 20 mL of 50:50 ethanol/water, 300 W Xe lamp, $\lambda > 400$ nm.	800 (AQY=7.3%)	[96]
CdS-Ti-MCM-48-21-MPTMS-25	0.04 g catalyst + 20 mL of 50:50 ethanol/water, 300 W Xe lamp, $\lambda > 400$ nm.	511 (AQY=13.8%)	[97]
CdS-Ti-MCM-48-21-25	0.04 g catalyst + 20 mL of 50:50 ethanol/water, 300 W Xe lamp, $\lambda > 400$ nm.	2726 (AQY=36.3%)	This work

Table 4. Summary of photocatalytic hydrogen evolution rate of fresh and recycled samples.

Sample	Hydrogen evolution rate of fresh (mmol/h/g _{catalyst})	Hydrogen evolution rate of recycling run 1 (mmol/h/g _{catalyst})	Hydrogen evolution rate of recycling run 2 (mmol/h/g _{catalyst})
CdS-Ti-MCM-48-21-25	2.726	2.562	2.435

Table 5. Textural properties of fresh and spent CdS-Ti-MCM-48-31-MPTMS-25 samples.

Material	Si/CdS ^a (mol)	Si/CdS ^b (mol)	Surface Area ^c ² -1 (m g)	Pore Volume ^d ³ -1 (cm g)	Pore Diameter ^e (Å)
CdS-Ti-MCM-48-21-25	25	40	1139	0.66	19.3
CdS-Ti-MCM-48-21-25-spent	25	43	1275	0.79	19.9

^a Molar ratio in the synthesis gel

^b Molar ratio in the product measured by the AAS study

^c Determined by applying the Brunauer-Emmett-Teller (BET) equation to a relative pressure (P/P_0) range of 0.05–0.30 to the adsorption isotherm

^d Calculated from the amount of nitrogen adsorbed at the highest relative pressure (P/P_0) ~ 0.98

^e Calculated from the Barrett-Joyner-Halenda (BJH) equation using the desorption isotherm