Investigation of Electron Transport Through Alkanedithoil of Functionalized Zn_3P_2 Nanowires for Hydrogen Production

Review Article

Li H[1*], Yu YH[1,2], Vasiraju V[1,2], Vaddiraju S[1,2], Cheng Z[1,2,3*]

[1] Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX, USA.
[2] Department of Materials Science & Engineering, Texas A&M University, College Station, TX, USA.
[3] Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX, USA.

Abstract

Surface modified Zn_3P_2 nanowires samples using alkanedithiol groups with different alkyl chain length were tested for hydrogen production. 1, 3-PDT exhibits the highest hydrogen production rate as 7288 ± 204 umol/h/g, which is 4 and 63 times higher than 1, 4-BDT and 1, 12-DDT respectively. The distance between photogenerated sites on Zn_3P_2 nanowires and top molecule of alkanedithiol groups affects hydrogen reduction activity. Hydrogen production rate depends on electron transfer rate and tunneling rate. Mechanism explained gives a comprehensive perspective on how to optimize the structure of the Zn_3P_2 nanowires and maximize the hydrogen reduction activity.

Introduction

Solar energy is a gigantic energy source with 3.0×10^{24} J a year, and world energy consumption is 5.0×10^{20} J a year [8]. With only 10% efficiency conversion of 0.1% solar energy would meet the demand of current energy need [14]. Hydrogen energy is considered as a "fuel of the future" due to its abundance and no greenhouse emissions [6]. Photoelectrochemical water-splitting process is a zero-emission process [1]. However, certain issues come up with photoelectrochemical water-splitting process such as inefficient use of solar spectrum, for example, composite such as TiO_2, $SrTiO_3$, $KTaO_3$, ZnO, ZnS_2 [5] can only absorb wavelength in UV region (5% of solar spectrum), and inefficient use of dissociated electrons and holes in catalysis.

Suitable catalysts for solar hydrogen production have to meet the following requirements [9]: 1. Visible light absorption. 2. High chemical stability. 3. Suitable band edge positions to enable reduction/oxidation of water. 4. Efficient charge transport in the semiconductor. 5. Low over potential for the reduction/oxidation reaction, and 6. Low cost [20]. While metallic oxides have large band gap (such as SnO_2, TiO_2) [17] that cannot use solar energy efficiently, sulfides oxides possess narrower band gaps leading to a higher absorption of sunlight [18]. However sulfides oxides are less stable in the water based solvent and can easily undergo photochemical oxidation reaction [13].

A novel material Zn_3P_2 nanowires has been studied intensively. Zn_3P_2 nanowire structure possesses suitable optical properties and band structure and therefore has one of the highest potentials for energy and least expensive among tested 23 compounds [21]. However, Zn_3P_2 nanowires suffer low stability which cause the degradation of Zn and therefore sacrifice its properties needed for the photochemical reactions [12]. However a novel vapor phase method [3] was reported to synthesise high-quality stable Zn_3P_2 nanowires. Moreover, exposing Zn_3P_2 nanowires to a vapor of the different organic functional groups immediately after obtaining Zn_3P_2 nanowires carried out functionalized Zn_3P_2 nanowires offers several advantages, such as resistance against degradation that caused by moisture and air [3].

By functionalizing the Zn_3P_2 nanowires using alkanedithiol groups with different alkyl chain length, the relations between molecular structure and the rate of electron transfer were investigated in this paper. Understanding how electrons transfer between functional groups and Zn_3P_2 nanowires would result in a comprehensive perspective on how to choose the functional groups to modify Zn_3P_2 nanowires that maximizes the photocatalytic activity of the Zn_3P_2 nanowires.

Requirements for hydrogen production from water splitting are to find an adequate electronic structure to absorb photons and produce excited electrons. During the process of water splitting, which leads to the creation of free electrons and holes within the

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nanowires, fast electron-hole recombination process [7] occurs. Therefore, strong reduction solvent such as methanol serves as a hole scavenger to avoid electron-hole recombination process and therefore the excited electrons are able to undergo the desired chemical reactions.

Experiments

Bulk Zn_3P_2 nanowires were synthesized by using chemical vapor deposition chamber as described in the reference [3]. And the functionalization of the bulk Zn_3P_2 nanowires was synthesized by exposing the Zn_3P_2 nanowires to a vapor of the different organic functional groups. In this experiment Zn_3P_2 nanowires were functionalized by using 1, 3-propanedithiol (1, 3-PDT), 1, 4-butanedithoil (1, 4-BDT) and 1, 12-dodecanedithio (1, 12-DDT) for study.

Figure 1 shows a schematic of functionalized Zn_3P_2 nanowires. All three functionalized Zn_3P_2 nanowires are characterized by scanning electron microscopy (SEM Quanta 600). Photocatalytic hydrogen evolution reaction was carried out in a 250 mL Pyrex water-jacketed round bottom flask. Firstly, 150 mL of methanol and Milli-Q water aqueous solution (20%/80% V/V) was mixed vigorously by a magnetic stirring bar, then aqueous solution was undergone 10 minutes ultra-sonication to remove any solved gases in the system. Secondly, Zn_3P_2 were introduced into 150 mL of methanol-Milli-Q water aqueous solution to obtain photocatalytic system, after which the system was degassed 30 minutes and N_2 gas was used to remove any oxygen in the system. The photocatalytic system was irradiated under a 300-watt xenon lamp (PE300BF, Cermax). Temperature of photocatalytic system was measured at 25°C by circulating cooling water using water recirculating cooling system. The amount of produced hydrogen was monitored, extracted by syringe, and analyzed at 30-minute intervals by gas chromatography (GC, Agilent 7820A) with a thermal conductivity detector equipped with a 5-Å molecular sieve column. The net weights of Zn_3P_2 nanowires were measured by removing Zn_3P_2 nanowires using ultra-sonication from the foil and then measuring the weight difference [18].

Results and Discussions

Figure 2. shows that amount of hydrogen produced monotonically increased with time under visible light irradiation, from different functionalized organic groups of Zn_3P_2 nanowires, which suggests a stable and active photocatalytic reaction. In a 4-hour test period, 1, 3-PDT exhibits the highest photocatalytic activity among all three different functional groups, followed by 1, 4-BDT and 1, 12-DDT respectively. Besides, the Zn_3P_2 nanowires functionalized by 1, 12-DDT showed gentle photocatalytic activity that is hard to be observed in Figure 2. For the first half hour, relatively small amounts of hydrogen were obtained for all the three different functional groups. This observation suggests that all functionalized Zn_3P_2 nanowires initially start with a process called a photochemical activation [22]. Subsequently, the hydrogen evolution reaction proceeds in a stable pace.

The hydrogen results in Figure 3 shows that hydrogen production rates with 4 hours over Zn_3P_2/1, 3-PDT, Zn_3P_2/1, 4-BDT, and Zn_3P_2/1, 12-DDT are 7288 ± 204, 1839 ± 35, and 155 ± 4 umol/h/g, respectively. The hydrogen production rate of 1, 3-PDT is approximately 4 times higher than that of 1, 4-BDT and 63 times higher than that of 1, 12-DDT respectively. The results indicate alkyl chain length have a significant impact on hydrogen production rate. The mechanism of this behavior is further discussed below.

Figure 4. shows the Scanning Electron Microscopy (SEM) images of the different functional groups before (abc) and after (def) hydrogen evolution reaction. As shown in Figure 4a, b and c, the functionalized Zn_3P_2 nanowires are kept in similar morphologies after the functionalization. Degradation of Zn_3P_2 nanowires occurs in all three functionalized groups after hydrogen evolution reaction. The degradation in morphology renders nanowires small particles combined with nanowires. This photo-catalytic degradation could be explained that Zn_3P_2 reacts with water as described by Equation (1): [3]

$$Zn_3P_2 + 6H_2O \rightarrow 3Zn(OH)_2 + 2PH_3 \qquad (1)$$
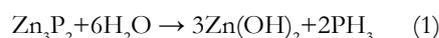
As shown in Figure 4, 1, 3-PDT was found to be the most stable among three different functionalized groups, since it showed the least amount of degradation, while 1, 12-DDT showed the highest amount of degradation. This could be explained due to the different surface coverage of Zn_3P_2 nanowires. Functional groups with shorter alkyl chain length occupy less volume in space; hence they possess larger percentage of surface coverage of Zn_3P_2 nanowires. Thus the Zn atom attached to functional groups are less subjected to water to form Zn hydroxide, and therefore this enhances the structure stability of Zn_3P_2 nanowires.

Figure 5 shows a possible hydrogen evolution mechanism and electron transfer direction on the functionalized Zn_3P_2 nanowires.

Figure 1. Schematic of functionalized Zn_3P_2 nanowires with alkanedithoil groups (1, 3-PDT, 1, 4-BDT, 1, 12-DDT).
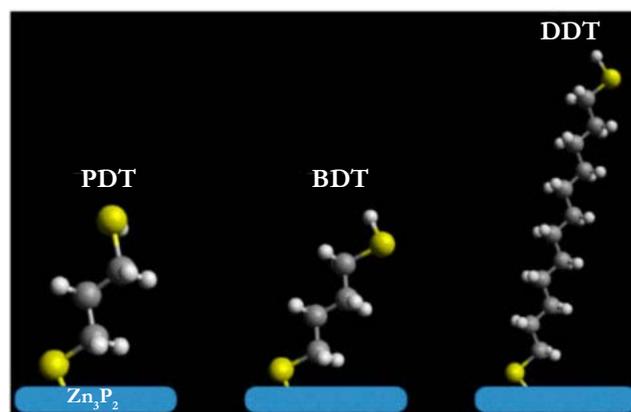
Figure 2. Photocatalytic hydrogen evolution reaction results using different organic functional groups of photocatalysts suspended in 150 mL methanol - Milli - Q aqueous solution (20%/80%V/V).
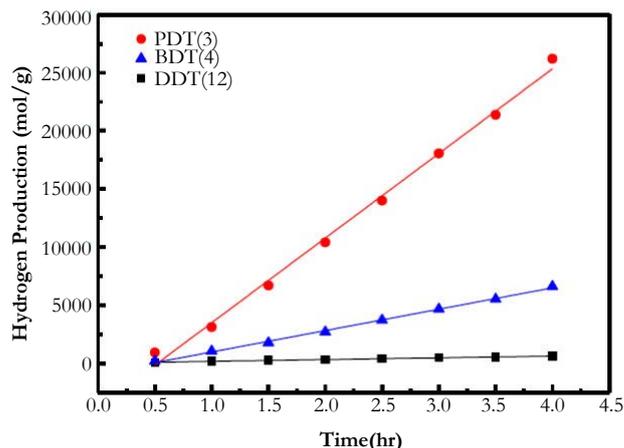

Figure 3. Photocatalytic hydrogen evolution results of the dependence of different functional groups amount on photocatalytic activity for hydrogen evolution.
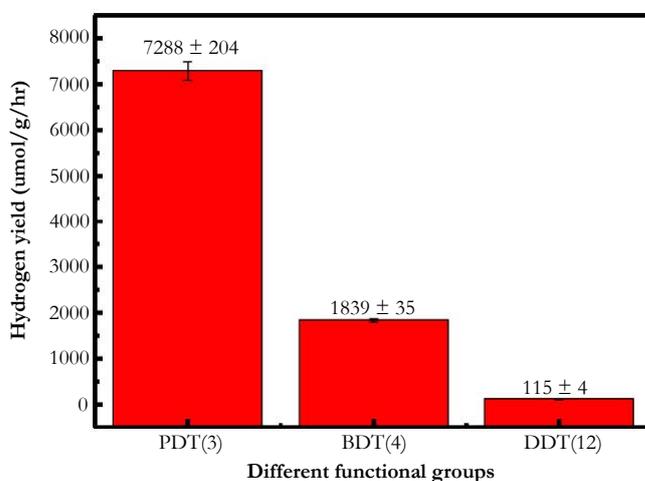

Figure 4. SEM images of Zn_3P_2-1, 3-PDT, Zn_3P_2-1, 4-BDT, and Zn_3P_2-1, 12-DDT respectively before (abc) and after (def) hydrogen evolution reaction.

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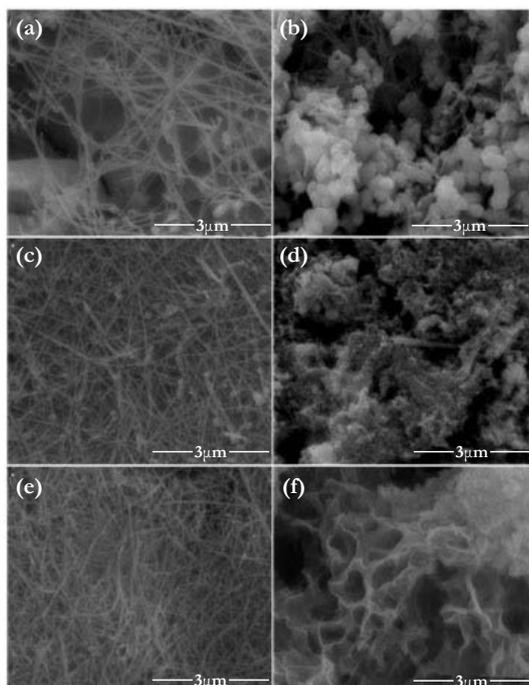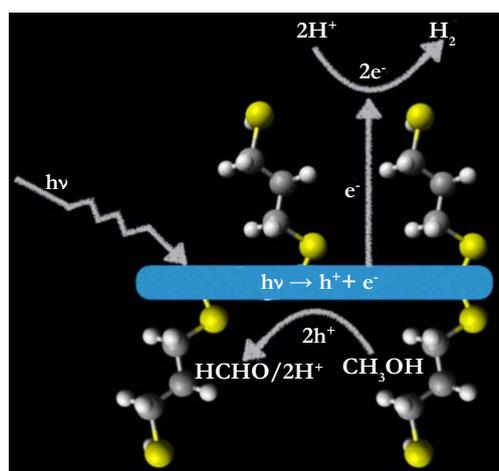
Figure 5. Schematic of electrons and holes transfer and redox reactions on the functionalized Zn$_3$P$_2$ nanowires.

The redox reaction on the functionalized Zn$_3$P$_2$ nanowires occurs at two different locations. Visible light is absorbed on the surface of Zn$_3$P$_2$ bulk nanowires and generates holes and free electrons; the reaction occurs as follows $h\nu \rightarrow h + e$. The photo-generated electrons is expected to transfer to the bond point of functional molecule, then they move along the organic functional group and end up at the top of the functional molecules, where the reaction of reduction of hydrogen ions occurs and leads to the formation of hydrogen, namely: $2H^+ + 2e \rightarrow H_2$. The photo-generated holes, on the other hand, stay on the surface site of bulk Zn$_3$P$_2$ nanowires, are not covered by organic functional groups, oxidizing methanol leading to the formation of formaldehyde and hydrogen ions: $2h^+ + CH_3OH \rightarrow HCHO + 2H^+$ [4, 16]. The surface of Zn$_3$P$_2$ nanowires has a high possibility that it is not entirely covered by the organic functional groups since the formation defects occur during the synthesis process of Zn$_3$P$_2$ nanowires as well as chemical vapor deposition process [15]. The rate of hydrogen production could be considered as the rate of electron transfer in this system.

The more electrons undergo the reaction of reduction of hydrogen ions, the higher is the rate of formation of hydrogen.

One of the possible mechanisms to explain the electron transfer rate across alkyl chain is the tunneling effect from Zn$_3$P$_2$ bulk nanowires to the end point of functional molecule. If an alkyl chain in a certain functional group is long, then the tunneling rate of that functional group is low [19]. Moreover, the rate of electron transfer (k_{ET}) on the Zn$_3$P$_2$ nanowires is exponentially related to the distance between photo-generated sites (donor) and the end point of functional molecule (acceptor); the relationship between the two is described by equation (2) (where k_0 is a pre-exponential factor; β is a structure-dependent attenuation factor that describes the decay of electronic coupling between donor and acceptor as the distance separating them increases; and $d_{D,A}$ is the distance separating the donor and acceptor) [10].

$$k_{ET} = k_0 e^{-\beta d_{D,A}} \tag{2}$$

The electron can transport from the Zn$_3$P$_2$ nanowires bulk surface to the molecule by tunneling, and the rate of electron transfer also has influence on the electron transfer. Therefore the total reaction rate is limited by the tunneling rate and rate of electron transfer in the case of long alkyl chain. This explanation agrees

with the experimental results, as the alkyl chain length increases in alkanedithoil functional groups, the hydrogen production rate decreases dramatically when the alkyl chain length reaches 12. Similarly, the current density decreases as the distance between photogenerated sites and the end point of functional molecule increases. The exponential decrease in current is consistent with the electron transport rate [2, 11], described by equation (3).

$$I = I_0 e^{-\beta d_{D,A}} \tag{3}$$

Since the reduction current is proportional to the hydrogen reduction rate, then the alkyl chain length is dependent to hydrogen production rate as well. This observation also agrees with the lower tunneling rate of long alkyl chain, since the current in a tunneling is proportional to the probability of tunneling. In short, those two factors, electron transfer rate and current rate that are in corresponding with tunneling rate, both contribute to lower hydrogen production rate for longer alkyl chain in alkanedithiol functional groups.

Conclusion

In summary, we modified Zn$_3$P$_2$ nanowire surface and investigated the relationship between hydrogen production rate and alkyl chain length in alkanedithiol functional groups. Hydrogen production activity was affected by the distance which is the length of alkyl chain between the photo-generated point on the Zn$_3$P$_2$ nanowires and the molecule at the end of functional groups. As the alkyl chain decrease, the hydrogen production rate increases, due to the increased rate of electron transfer as well as vigorous tunneling effect, which ultimately enhanced the charge separation. By changing the alkyl chain length of functional groups, we assume the desired functionalized Zn$_3$P$_2$ nanowires such as EDT (1, 2-Ethanedithiol) could be further tested hydrogen production rate and structure stability in the future. Therefore, highly effective functionalized Zn$_3$P$_2$ nanowires was produced, which could be further modified structurally to obtain higher hydrogen production rate.

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