Photocatalytic Hydrogen Production from Seawater Using CdxZn1-xS

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Abstract—**Hydrogen gas has been shown to photocatalytically generated from pure water. With saltwater comprising 93% of the earth's water reservoir, methods to produce hydrogen from seawater minus the expensive water purification are desired. $Cd_{0.8}Zn_{0.2}S$ has been proven as an effective photocatalyst for hydrogen production but it remains to be tested in seawater. This study provides proof of concept for hydrogen production from seawater using fresh and reused $Cd_{0.8}Zn_{0.2}S$ upon irradiation with visible light and with the addition of sulfide/sulfite as sacrificial agents. The post-usage characteristics of $Cd_{0.8}Zn_{0.2}S$ catalyst were investigated using SEM and FTIR. The rate of hydrogen gas production from seawater was up to six times faster than in distilled and simulated seawater for both fresh and reused catalyst. Reused catalyst showed reduced rates of gas accumulation. Catalysts exposed to non-distilled water showed marked changes in their SEM appearance and their spectral transmittance.**

Index Terms—**Hydrogen production, photocatalyst, seawater, visible light.**

I. INTRODUCTION

The rapid depletion of the earth's energy sources such as coal and petroleum products and the problems that they pose to the environment have led to the shift towards alternative and renewable fuels for energy production. Hydrogen is a promising fuel because it is pollution free and it has a high energy yield [1]. Most of the hydrogen is produced via steam reforming of petroleum and natural gas however, this is not sustainable in the near future [1]. Other methods for hydrogen production are water electrolysis and the

photocatalytic water splitting. Photocatalytic production of hydrogen from natural resources such as solar energy and water is promising because these resources are abundant and have a better impact to the environment.

The photocatalytic hydrogen generation using pure water has been widely investigated in the past years. Although the Earth is 71% water, 93% is saltwater. Saltwater might be a better source of hydrogen since it would not need to undergo purification. However, there have been few studies for hydrogen generation using seawater. Some studies have used different catalysts such as $ZnS_{1-x}-0.5yO_x(OH)_y$-ZnO [2], CdS/TiO_2 [3], $Pt/Cd_{0.5}Zn_{0.5}S$ [4] using visible light [5] and UV light [6]. Most studies have used artificial saltwater with certain amount of salts and ions dissolved, while Lee *et al.* have used natural seawater from the Pacific Ocean. Li *et al.* have reported that hydrogen production increases at a higher NaCl concentration over $ZnS_{1-x-0.5y}O_x(OH)_y$-ZnO photocatalyst, however, at low NaCl concentrations, hydrogen production is lower in saltwater than that in seawater [5]. The development of a stable and effective photo catalyst for hydrogen production in seawater is still a work in progress. Potential problems that are expected to arise from the use of saltwater or seawater for photocatalytic hydrogen production include reduction in photocatalytic efficiency due to deposition and corrosion.

When light strikes a metal, a photon excites the electron, allowing it to jump from the valence band to the conduction band. This creates an electron – hole pair, which triggers the redox reactions In this case, hydrogen gas is the product of the reduction reaction and oxygen gas is the product of the oxidation reaction. In order to produce hydrogen using visible light irradiation, the photocatalyst must satisfy band requirements and its band gap must be narrow enough to absorb visible light. Also, the efficiency of the photocatalytic water splitting is reduced by the fast electron – hole recombination and the backward reaction of hydrogen and oxygen to form water.

In order to arrive at an effective photocatalytic hydrogen production method, the right photo catalyst must be used. $Cd_xZn_{(1-x)}S$ has been proven effective for hydrogen reduction [7]. It is visible light active and it has a narrower band gap compared to metal oxides such as TiO_2 [1]. Also, $Cd_xZn_{(1-x)}S$ does not need an expensive metal co-catalyst thus proving that it may be a cheaper option.

In order to enhance the efficiency of photocatalytic hydrogen production, the fast recombination of electron – hole recombination must be minimized. To do this, sacrificial reagents such as methanol [6], glucose [4] and sulfide ions [2] have been added to the aqueous suspension containing the photo catalyst. These reducing agents, that are also called

hole scavengers, are irreversibly oxidized by photogenerated holes. Due to this phenomenon, the electron hole recombination is reduced and the efficiency of hydrogen production is enhanced [8]. However, the sacrificial reagents get depleted in the process and this may limit the production of hydrogen. Sacrificial reagents that are naturally abundant in the environment or present as industrial pollutants are more practical.

In order to develop a continuous and efficient process for the photocatalytic hydrogen generation using seawater, there is a need for a stable and effective photo catalyst for hydrogen production. If this is satisfied, then there is no longer need to produce or regenerate the photo catalyst frequently while still attaining high hydrogen production levels. Hydrogen produced from seawater could be used as a fuel to generate electricity in the remote islands. The product of the hydrogen and oxygen combination could produce clean and desalinated water (H_2O).

In this study, the photocatalytic hydrogen production from seawater using $Cd_xZn_{(1-x)}S$ is investigated. The hydrogen production in pure water, artificial saltwater and natural sea water is compared. The effect of continued and repeated usage to the production rate and to the catalyst is also determined. The production and characterization of the $Cd_xZn_{(1-x)}S$ photocatalyst, including the determination of its band gap energy, were done by Doon *et al.* [7] and is not part of this study.

II. MATERIALS AND METHODS

A. Materials

The $Cd_{0.8}Zn_{0.2}S$ photocatalyst used in this study was synthesized using the co – precipitation method [7]. Cadmium acetate dehydrate $Cd(CH_3COO)_2\text{-}2H_2O$ and zinc acetate dihydrate $Zn(CH_3COO)_2\text{-}2H_2O$ were dissolved in 100 mL deionized water and was constantly stirred. 0.1 M sodium sulfide $Na_2S\text{-}H_2O$ was added drop wise. The Cd:Zn:S atomic ratio that is used is 0.8:0.2:1. The precipitate that was formed in the reaction was separated from the solution by vacuum filtration, washed with deionized water, and 348 K for eight (8) hours, and was found to have a band gap energy of 2.25 eV [7].

B. Types of Water

There were three types of water that was used, namely, distilled water, artificial (simulated) saltwater, and natural seawater from Bolinao, Pangasinan. The distilled water used was Nature Spring Distilled Drinking Water. The artificial saltwater was prepared by dissolving inorganic salts (NaCl, 27.21 g; $MgCl_2$, 3.81 g; $MgSO_4$, 1.66 g; $CaSO_4$, 1.404 g; K_2SO_4, 0.577 g; K_2CO_3, 0.212 g; KBr, 0.1034 g) in 1.00 L of distilled water. The natural seawater was collected from the Bolinao Marine Laboratory, Bolinao, Pangasinan.

C. Hydrogen Production

0.100 g of $Cd_{0.8}Zn_{0.2}S$ photo catalyst was dispersed in 100 mL water. 0.96 g $Na_2S\text{-}H_2O$ and 1.26 g Na_2SO_3 was added in the solution as sacrificial reagents. The solution was placed in a gas tight Pyrex cylindrical vessel with an O-ring joint seal. The reactor was purged with nitrogen gas for fifteen (15) minutes to remove oxygen. The reactor was irradiated on one side with a 300 W tubular halogen lamp for six (6) hours. After six hours of continued usage, the solution was filtered using a 0.45 μm cellulose membrane and a Buchner funnel. The photo catalyst was reused and dispersed in 100 mL of fresh distilled water, salt water or sea water. The reactor was again purged with nitrogen gas for fifteen (15) minutes and irradiated for another six (6) hours.

D. Hydrogen Gas Sampling

The amount of hydrogen produced was determined by taking hourly samples from the reactor headspace for six (6) hours. 1-mL gas samples w taken from the reactor headspace through the PTFE septum using a 2.5 mL gas tight syringe (Hamilton HD-type). The gas sample was injected manually into a gas chromatograph (GC) equipped with a thermal conductivity detector (Shimadzu GC-TCD 2014) with a molecular sieve column (Supelco Mol Sieve 5A). Nitrogen was used as the carrier gas.

E. Determination of the Rate of Hydrogen Production

A calibration curve was made by injecting various amounts of 1% $H_2\text{-}N_2$ onto the gas chromatograph to relate the chromatogram peak area to the amount of hydrogen in micromoles. The calibration curve was used to determine the amount of hydrogen in the sample. Every hour, three samples were taken and analyzed in the gas chromatograph equipped with a thermal conductivity detector (GC – TCD). After finishing all the runs for the catalyst, another trial (Trial 2) performing the same conditions was done in order to confirm the validity of the results. The average amount of hydrogen present in the reactor headspace in trial 1 and trial 2 was taken and plotted against the number of hours of usage of the catalyst.

F. Post-usage Catalyst Characterization

The catalyst was characterized after usage in order to determine if there were possible changes to the catalyst after usage in saltwater and seawater. After a total of 12 hours of usage, the catalyst was filtered using a 0.45 μm cellulose membrane, Buchner funnel and dried. In order to investigate the possible surface modifications of the catalyst, SEM micrographs of the used photo catalyst was taken using a Hitachi Scanning Electron Microscope S-3400N. The infrared spectra of the used photo catalyst was taken using a Thermo – Scientific Fourier Transform Infrared Spectra (FTIR) in order to investigate the possible changes in the composition of the catalyst.

III. RESULTS AND DISCUSSION

A. Hydrogen Production

The hydrogen produced from the seawater is greater than the hydrogen produced from the saltwater and seawater. At hour 6, the amount of hydrogen in the reactor headspace was 0.0882 mmol/L for the photocatalyst seawater while only 0.0369 mmol/L for the saltwater and 0.0163 for the distilled water. After hour 6, the catalyst was recovered and filtered and a fresh solution was prepared thus the amount of the hydrogen present in the reactor headspace went back to zero. The amount of hydrogen in the reactor headspace for the reused catalyst is also linearly increasing, as can be seen from

Fig. 1. However, for the repeated usage, the amount of hydrogen produced decreased as compared to the amount of hydrogen produced in the first six hours. The amount of hydrogen in the reactor headspace upon irradiation of the reused catalyst for another six (6) hours was 0.0776 mmol/L for the seawater, 0.0247 mmol/L for the saltwater and only 0.00242 mmol/L for the catalyst in distilled water.

The amount of hydrogen present in the reactor headspace is linearly increasing from the first to the sixth hour, as can be seen from Fig. 1. Since the slope of the hydrogen produced is constant, the hydrogen production rate per hour is equal to the slope of the line. 0.016 mmol/L per hour was produced using seawater while only 0.0059 mmol/L/hr and 0.0025 mmol/L/hr was produced using saltwater and pure distilled water respectively. The hydrogen production in seawater was 2.75 times that in saltwater and 6.3 times that in pure distilled water. After 6 hours of usage, recovery of catalyst and irradiation in a fresh solution, the hydrogen production rate decreased by 34.7% and 33.9% in seawater and saltwater, respectively. Noetheless, the production for both types of water was still considerably high. fThe production rate in pure distilled water decreased by 88.3%, lowering the production rate to 0.00043 mmol/L/hr. This suggests that the $Cd_{0.8}Zn_{0.2}S$ catalyst was more stable in seawater.
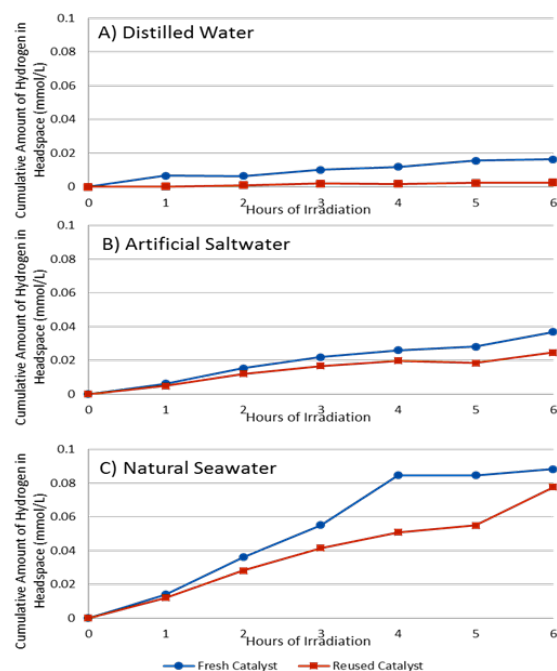

Fig. 1. Cumulative amount of hydrogen in reactor headspace (mmol/L) of the fresh and reused catalyst in A) distilled water, B) artificial saltwater and C) natural seawater.
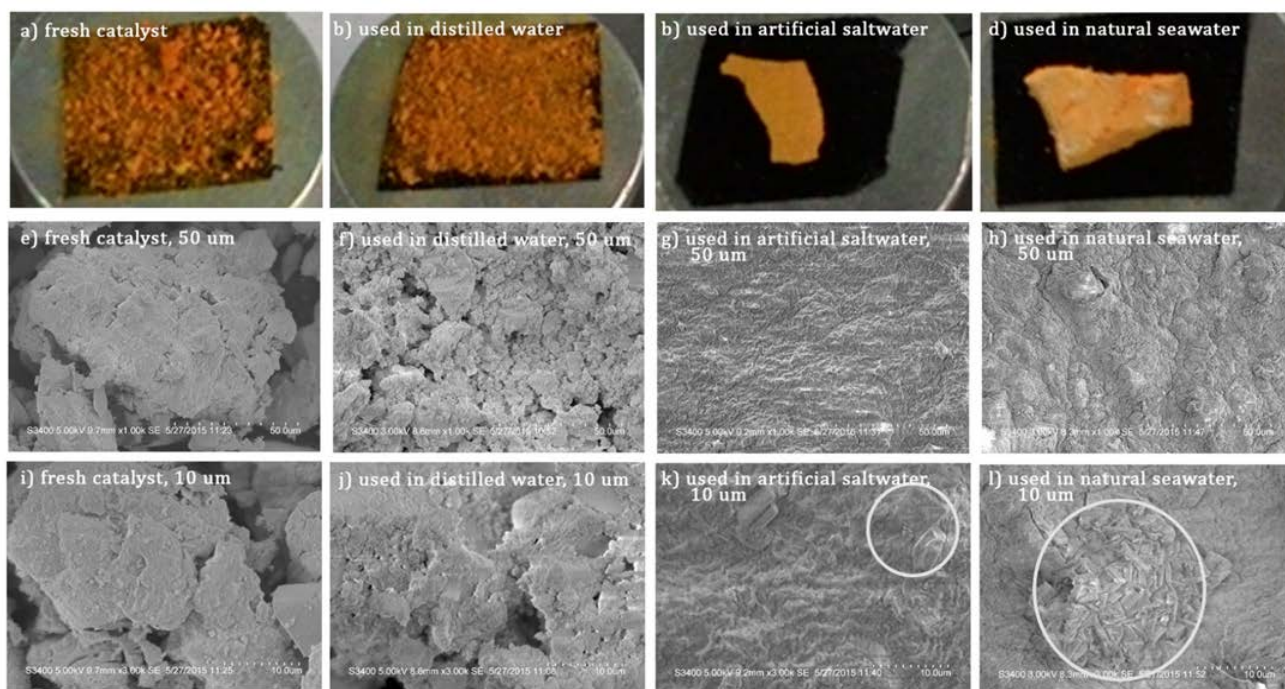

Fig. 2. Photographs and SEM images of the fresh and used catalyst. A to D are photographs of the fresh catalyst (A), used catalyst in distilled water (B), used catalyst in artificial saltwater (C), used catalyst in natural seawater (D). E-H are SEM photographs with 1k magnification and 50um of the fresh catalyst (E), used catalyst in distilled water (F), used catalyst in artificial saltwater (G), used catalyst in natural seawater (H). I-L are SEM photographs with 1k magnification and 50um of the fresh catalyst (I), used catalyst in distilled water (J), used catalyst in artificial saltwater (K), used catalyst in natural seawater (L).

B. Post-usage Characterization

The catalyst after usage in saltwater and seawater became clay – like while the catalyst used in distilled water remained grainy like the fresh catalyst as can be seen in the photographs in Fig. 2 (A-D). As shown in the SEM photographs of the fresh at used catalyst at 50 microns in Fig. 2 (E-H), the catalyst after use in seawater (H) and saltwater (G) is more compact and does not form small flakes or grains.

Upon a closer look at the SEM photographs at 10 microns, it can be seen from Fig. 2 (I-L) that there are rectangular crystalline structures deposited on the surface of the catalyst (K, L). However, these components were not identified because the catalyst was not tested using SEM – EDX. It could only be inferred that these crystalline structures could be salt deposits.

FTIR is a useful test to determine the present components and characteristic bonds based on the resulting characteristic

peaks at certain wave numbers. Upon analysis of the FTIR spectra of the fresh and used catalyst in Fig. 3, it is evident that the catalyst, after use in distilled water, did not change much in its composition. However, there are noticeable peak splitting and shifting, which likely indicates a change in the metal-sulfide bond. Possibilities include

1) a replacement in the cation, (although this is unlikely, since the only other cation present known is Na+) or
2) a weak anodic photodecomposition of the catalyst, breaking the CdZnS bond to separate CdS and/or ZnS bonds.
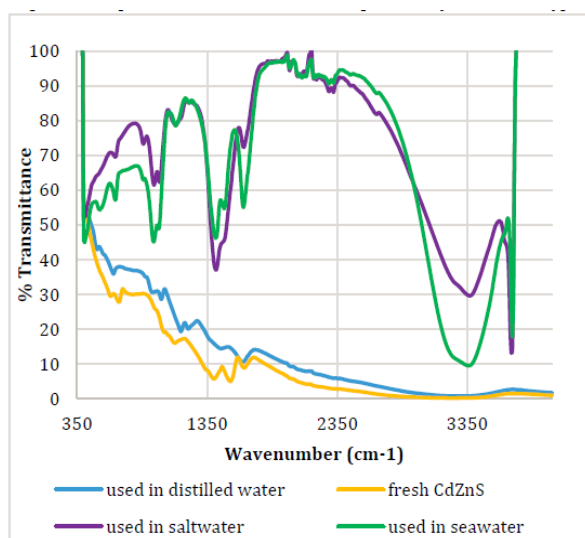3) a change in the adsorbed ion species on the catalyst surface

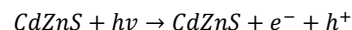Fig. 3. FTIR spectra of fresh and used CdZnS photocatalyst in various types of water.

The drastic change in the catalyst after use in seawater is evident. While some peaks are retained, such as those in ~650 nm, ~920 nm, ~1400 nm, and the ~1620 nm, the majority are completely different. Based on the characteristic frequencies of polyatomic inorganic ions [9], the following species may be present in the catalyst: sulfate, dibasic phosphate, bisulfite, monobasic phosphate, sulfite, chlorite, thiosulfate, ammonium, water of crystallization and carbonate. Sulfite and thiosulfate species notably have a near exact match in their peaks. However, both anions are soluble in cations present in saltwater, which indicates that these peaks are not a result of precipitation. This indicates that there is a change in the identity of the sulfide portion of the catalyst into the two said species, but the change is unknown whether by photocatalytic oxidation or by replacement with the ions in solution.

The catalyst used after saltwater and seawater are also very similar, despite a significant difference in hydrogen production. The absence of a peak at ~520 nm and the weaker magnitude of two consecutive peaks from ~1450 to ~1650 nm in simulated saltwater-used catalyst may possibly explain this difference, however it is more likely that there exists a co-catalyst in seawater that greatly enhances the photocatalyst activity since the complete composition of the seawater is not available. The greater relative magnitudes of the peaks in seawater-used catalyst indicate that there is an enhancement in the functional groups adsorbed in the catalyst.
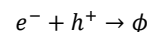
Building on the work of Tambago and deLeon, [10], possible reactions using the components from artificial saltwater are listed:
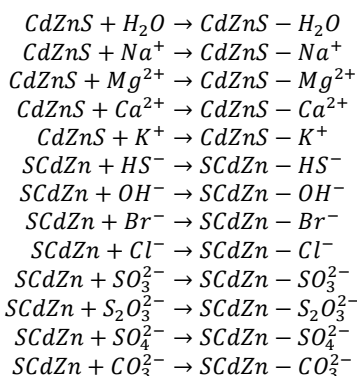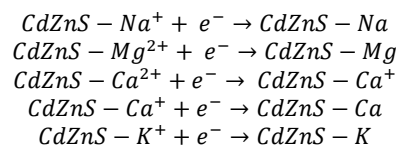
Photocatalytic reactions
Absorption of photon

$$CdZnS + hv \rightarrow CdZnS + e^- + h^+$$

Recombination of electron and hole

$$e^- + h^+ \rightarrow \phi$$

Adsorption

$$CdZnS + H_2O \rightarrow CdZnS - H_2O$$
$$CdZnS + Na^+ \rightarrow CdZnS - Na^+$$
$$CdZnS + Mg^{2+} \rightarrow CdZnS - Mg^{2+}$$
$$CdZnS + Ca^{2+} \rightarrow CdZnS - Ca^{2+}$$
$$CdZnS + K^+ \rightarrow CdZnS - K^+$$
$$SCdZn + HS^- \rightarrow SCdZn - HS^-$$
$$SCdZn + OH^- \rightarrow SCdZn - OH^-$$
$$SCdZn + Br^- \rightarrow SCdZn - Br^-$$
$$SCdZn + Cl^- \rightarrow SCdZn - Cl^-$$
$$SCdZn + SO_3^{2-} \rightarrow SCdZn - SO_3^{2-}$$
$$SCdZn + S_2O_3^{2-} \rightarrow SCdZn - S_2O_3^{2-}$$
$$SCdZn + SO_4^{2-} \rightarrow SCdZn - SO_4^{2-}$$
$$SCdZn + CO_3^{2-} \rightarrow SCdZn - CO_3^{2-}$$

Reactions on the catalyst surface
Reduction
Reduction – photodeposition

$$CdZnS - Na^+ + e^- \rightarrow CdZnS - Na$$
$$CdZnS - Mg^{2+} + e^- \rightarrow CdZnS - Mg$$
$$CdZnS - Ca^{2+} + e^- \rightarrow CdZnS - Ca^+$$
$$CdZnS - Ca^+ + e^- \rightarrow CdZnS - Ca$$
$$CdZnS - K^+ + e^- \rightarrow CdZnS - K$$

Production of hydrogen radical

$$CdZnS - H_2O + SCdZn + e^- \rightarrow CdZnS - H \cdot + SCdZn - OH^-$$
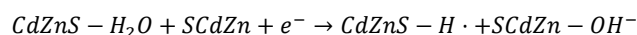
Metal-induced production of hydrogen radical

$$CdZnS - Na + CdZnS - H_2O + CdZnS$$
$$\rightarrow (CdZnS)_2 - NaOH + CdZnS - H \cdot$$
$$CdZnS - Mg + CdZnS - H_2O$$
$$\rightarrow (CdZnS)_2 - MgOH + CdZnS - H \cdot$$
$$CdZnS - Ca + CdZnS - H_2O$$
$$\rightarrow (CdZnS)_2 - CaOH + CdZnS - H \cdot$$
$$CdZnS - K + CdZnS - H_2O \rightarrow CdZnS - KOH + CdZnS - H \cdot$$

Hydrogen Production

$$2\ CdZnS - H \cdot \rightarrow 2\ CdZnS + H_2$$
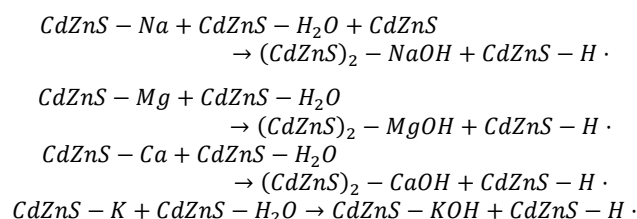
Oxidation
Bisulfide to disulfide

$$SCdZn - HS^- + h^+ \rightarrow SCdZn - HS \cdot$$
$$SCdZn - HS \cdot + SCdZn - OH^- \rightarrow CdZnS + SCdZn - S \cdot^- + H_2O$$
$$SCdZn - HS \cdot + SCdZn - S \cdot^- \rightarrow SCdZn - HS_2^- + CdZnS$$
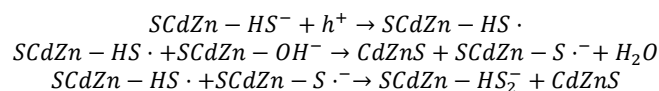
Sulphite to sulphur trioxide

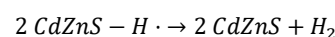$$SCdZn - SO_3^- + h^+ \rightarrow SCdZn - SO_3$$
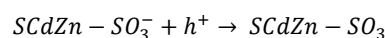
Sulphite to bisulphate

$$SCdZn - SO_3^{2-} + h^+ \rightarrow SCdZn - SO_3^-$$
$$SCdZn - SO_3^- + SCdZn - OH^- \rightarrow SCdZn - HSO_4^{2-}$$
$$SCdZn - HSO_4^{2-} + h^+ \rightarrow SCdZn - HSO_4^-$$

$$SCdZn - SO_3 + SCdZn - OH^- \rightarrow SCdZn - HSO_4^-$$
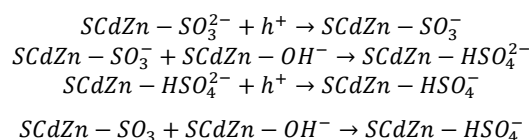
Sulphite to thiosulfate

$$SCdZn - SO_3^- + SCdZn - HS \cdot \rightarrow SCdZn - HS_2O_3^- + SCdZn$$
$$SCdZn - SO_3^- + SCdZn - HS^- \rightarrow SCdZn - HS_2O_3^{2-} + SCdZn$$
$$SCdZn - HS_2O_3^{2-} + h^+ \rightarrow SCdZn - HS_2O_3^-$$
$$SCdZn - SO_3 + SCdZn - HS^- \rightarrow SCdZn - HS_2O_3^- + SCdZn$$

Hydroxide to peroxide

$$SCdZn - OH^- + h^+ \rightarrow SCdZn - OH \cdot$$
$$2\,SCdZn - OH \cdot \rightarrow SCdZn - H_2O_2 + SCdZn$$

Halide to halogen

$$SCdZn - Br^- + h^+ \rightarrow SCdZn - Br \cdot$$
$$SCdZn + Cl^- \rightarrow SCdZn - Cl^- + h^+ \rightarrow SCdZn - Cl \cdot$$

$$SCdZn - Br \cdot + SCdZn - Br \cdot \rightarrow SCdZn - Br_2 + SCdZn$$
$$SCdZn - Cl \cdot + SCdZn - Cl \cdot \rightarrow SCdZn - Cl_2 + SCdZn$$

Hydrogen halides

$$SCdZn - Br \cdot + SCdZn - H \cdot \rightarrow SCdZn - HBr + SCdZn$$
$$SCdZn - Cl \cdot + SCdZn - H \cdot \rightarrow SCdZn - HCl + SCdZn$$

Desorption

$$SCdZn - HS_2^- \rightarrow CdZnS + HS_2^-$$
$$SCdZn - HSO_4^- \rightarrow SCdZn + HSO_4^-$$
$$SCdZn - HS_2O_3^- \rightarrow SCdZn + HS_2O_3^-$$
$$SCdZn - H_2O_2 \rightarrow SCdZn + H_2O_2$$
$$SCdZn - Cl_2 \rightarrow SCdZn + Cl_2$$
$$SCdZn - Br_2 \rightarrow SCdZn + Br_2$$
$$SCdZn - HCl \rightarrow SCdZn + HCl$$
$$SCdZn - HBr \rightarrow SCdZn + HBr$$

Liquid-phase reactions

$$HS_2^- + SO_3^{2-} \rightarrow S_2O_3^{2-} \rightarrow S_2O_3^{2-} + HS^-$$
$$S^{2-} + H_2O \rightarrow HS^- + OH^-$$
$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$$

From these, it can be seen that the presence of metal ions can possibly increase the rate of hydrogen production by increasing the amount of hydrogen radicals adsorbed on the surface of the catalyst.

However, despite the increase in the number of species that compete for vacant sites on the catalyst and despite the increase in possible side reactions such as production of hydrogen halides, the hydrogen production remains the dominant reduction reaction. The only reduction pathway is that of hydrogen production. Hydrogen halides are quickly re-dissolved in the basic aqueous solution upon formation. The other alternative, CO_2 production from the reduction of carbonate is not observed in the results from the gas chromatograph. The dominant oxidation reaction cannot be determined without an analysis of the seawater composition.

IV. Conclusion and Recommendations

This study demonstrated that regardless of whether the catalyst was fresh or reused, hydrogen gas production was greatest from seawater relative to the distilled and artificial seawater. In fact, the rate of hydrogen production using the fresh catalyst in seawater is 6.3 times that of distilled water and 2.75 times that of saltwater. The rate of hydrogen gas production was less when using reused catalyst, although

such decrease was least in natural seawater as a medium. The rate of hydrogen production using distilled water showed an 88% decrease, lowering the rate to 0.43 umol/L/hr from 2.5 umol/L/hr when the catalyst was reused. This suggests that the catalyst is more stable in seawater than in pure water.

The SEM appearance, as well as the spectral transmittance (FTIR) attributes of the catalyst exposed to the natural and artificial seawater changed significantly compared with the distilled water, which also showed close similarity to the unexposed (fresh) catalyst. There is a component in the natural seawater that may have enhanced the hydrogen production using seawater up to 6.3 times that of distilled water.

It is recommended to characterize and analyze the seawater to identify the components that may have enhanced the production of hydrogen. Focused studies on varying the concentration of the components of seawater must be done in order to determine their individual effects on the rate of hydogen production. The photodeposited salts in the catalyst must also be analyzed using SEM-EDX. Kinetic modeling on the hydrogen production using seawater should be done for the development of the continuous photocatalytic reactor.

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