

# Blue-photodecomposition of hydrazine in aqueous solution for H<sub>2</sub> production by using CdS photocatalyst

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## Abstract

**BACKGROUND:** Water dosed with hydrazine was used for the generation of H<sub>2</sub> via a photocatalytic process using CdS nanofibers as photocatalysts under blue light irradiation sources. The optimal dose for the highest H<sub>2</sub> production rate was obtained. Ethanol and sulfite/sulfide ions were also tested as hole scavengers.

**RESULTS:** CdS is semiconductor capable of absorbing blue light and used as a photocatalyst in H<sub>2</sub> production. The H<sub>2</sub> evolution with low doses of hydrazine was higher in comparison with the others sacrificial electron donors (SEDs). The mechanism of H<sub>2</sub> evolution involves the participation of hydrazine and the positive holes photogenerated on CdS photocatalysts.

**CONCLUSION:** H<sub>2</sub> is generated from the water–hydrazine solution in an O<sub>2</sub>-free system. Hydrazine in aqueous solution is photodecomposed by the holes, whereas H<sup>+</sup> is reduced to produce H<sub>2</sub> by the reaction with the conduction band electrons. Hydrazine as a sacrificial electron donor is better than the other reagents.

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**Keywords:** CdS; water–hydrazine; hydrogen production; hole scavenger; sacrificial electron donor (SED)

## INTRODUCTION

The photocatalytic H<sub>2</sub> generation from water by using multicomponent semiconductor catalysts under UV, visible or solar light energy sources<sup>1</sup> is typically conducted in the presence of sacrificial electron donors (SEDs) such as lactic acid,<sup>2</sup> formic acid,<sup>3</sup> alcohol molecules (methanol/ethanol/glycerol),<sup>4–7</sup> amine molecules (EDTA/TEOA),<sup>8,9</sup> or sulfite/sulfide ions among others.<sup>10–12</sup> It has also been reported that improved H<sub>2</sub> generation can be obtained using SEDs accompanied by dye contaminants (Methylene Blue, Methyl Orange or Eosyn-Y).<sup>8,13,14</sup> In comparison with different SEDs, sulfite (SO<sub>3</sub><sup>2-</sup>) ions have been proposed as the best SEDs for H<sub>2</sub> generation when Pt-CdS nanorods were used,<sup>15</sup> which was attributed to the highest oxidation potential of the sulfite ions, however, depending on the reaction conditions, by using NiO-CdS, the hole scavenging process was improved when methanol was used in the presence of NaOH, which involves the formation of the hydroxyl (•OH) radical as intermediate product, eliminating the competitive electron–hole recombination and increasing the H<sub>2</sub> evolution.<sup>16</sup> Therefore, the selection of a good SEDs depends on the interaction between the SEDs and semiconductor surface and reaction conditions (pH solution). Extensive research has demonstrated that nanostructured CdS is a good semiconductor for the H<sub>2</sub> production because it has specific band-gap energy of 2.4 eV, which allows the absorption of blue light irradiation. The position of its conduction band is negative enough to reduce the protons (H<sup>+</sup>) to produce H<sub>2</sub>.<sup>17–21</sup> On the other hand, hydrazine has been used either as 'oxygen scavenger' or 'hole scavenger' combined with methanol for the photocatalytic H<sub>2</sub> evolution using

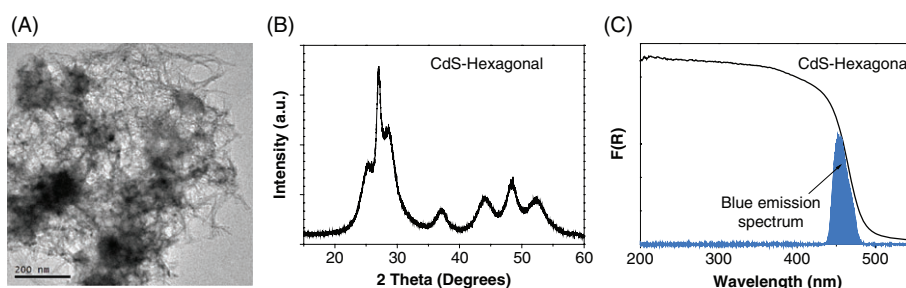
noble metal nanoparticles on TiO<sub>2</sub> photocatalysts.<sup>22</sup> Nowadays, hydrazine in aqueous solution has been used as SEDs with either Pt/TiO<sub>2</sub> or Au/TiO<sub>2</sub> photocatalysts under UV light irradiation,<sup>23,24</sup> where the noble metal nanoparticles play an important role for the photodecomposition of hydrazine, achieving high H<sub>2</sub> production. H<sub>2</sub> evolution from hydrazine has been also reported by photoelectrochemistry in a twin-compartment cell under visible light irradiation using a Pt-ITO/fullerene/Zn-phthalocyanine system,<sup>25</sup> where a Pt wire acted as a co-catalyst.

To understand the mechanism of the photocatalytic process of H<sub>2</sub> evolution from water contaminated with hydrazine, CdS nanofibers were used as photocatalysts. The kinetic study of hydrazine photodecomposition in aqueous solution in either O<sub>2</sub>-free or open-air systems (dissolved O<sub>2</sub>) was investigated. The structural, optical and morphological properties of CdS were obtained by means of XRD, DRS and TEM analyses. The hydrazine

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**Figure 1.** (A) TEM image, (B) X-ray diffraction, and (C) diffuse reflectance spectrum of CdS nanofibers.

doses were varied from 4 to 200 mmol L<sup>-1</sup> in order to obtain the optimal concentration for the highest H<sub>2</sub> production rate. The efficiency for the H<sub>2</sub> evolution with hydrous hydrazine was compared with ethanol and sulfite/sulfide solutions as SEDs. The possible formation of •OH radicals in the H<sub>2</sub> evolution under blue-light irradiation was investigated by study of the hydroxyterephthalic acid fluorescence spectrum, which was carried out in either O<sub>2</sub>-free or open-air systems. The photodecomposition mechanism of hydrazine in aqueous solution was discussed as a function of the photogenerated holes formed on the CdS nanofibers.

## EXPERIMENTAL SECTION

### Synthesis of the CdS

The CdS was synthesized by the precipitation method under mild synthesis conditions in a mixture of solvents containing 10 vol% of H<sub>2</sub>O, 60 vol% of ethylenediamine (EN, Aldrich) and 30 vol% of 1-butanol (JT Baker).<sup>17</sup> An appropriate amount of Cd(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O (Reasol) was first dissolved in a butanol–H<sub>2</sub>O solution at room temperature, constant stirring, adding EN at the end. Afterwards, carbon disulfide (CS<sub>2</sub>, Aldrich) was added dropwise, maintaining a molar ratio stoichiometry of S:Cd of 1:1, and the transparent mixture solution was heated at boiling point (110–120 °C) under vigorous magnetic stirring for 2 h and subsequently cooled at room temperature. Finally, the resulting yellow precipitate was collected by filtration, washed by ethanol–water solution and dried at 80 °C for 1 h.

### Characterization of CdS

CdS was characterized by X-ray powder diffraction using an X-ray diffractometer Siemens D500 with Cu K $\alpha$  radiation (50 kV, 40 mA). The scanning rate was 0.03° s<sup>-1</sup> in the 2 $\theta$  range from 5 to 70°. The band-gap energy was calculated using the Kubelka–Munk method from the diffuse reflectance spectra obtained with a Varian Cary-100 spectrometer equipped with an integration sphere. The morphology was determined by transmission electron microscopy (TEM) using a JEOL TEM 1230 microscope operated at 100 keV.

### Photocatalytic H<sub>2</sub> production system

The H<sub>2</sub> production reaction was carried out in a glass home-made photoreactor without any cooling system. The reactor was filled with 200 mL of an aqueous solution using different sacrificial electron donors (SEDs): (a) 0.1 mL (0.4 mmol L<sup>-1</sup>) to 5 mL (200 mmol L<sup>-1</sup>) of hydrazine hydrate (Aldrich); (b) 100 mL (3.5 mol L<sup>-1</sup>) of ethanol (JT Baker); and (c) 0.1 mol L<sup>-1</sup> of Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> (Reasol) in aqueous solutions. In all cases, 20 mg (0.1 g L<sup>-1</sup>) of the CdS powder were added as photocatalysts. The suspension was irradiated with four

blue LED lamps (12 W, 190 lumens each) placed close to the glass photoreactor in appropriate positions to ensure full illumination.<sup>26</sup> When either ethanol or sulfite/sulfide solution was used, the system was bubbled with N<sub>2</sub> before the blue-irradiation to simulate the O<sub>2</sub>-free system (reduced pressure of O<sub>2</sub>). Then, the system was sealed and the blue LED lamp turned on. On the other hand, when hydrazine was used, prior to the blue-irradiation, the water solution containing CdS powder was first bubbled with N<sub>2</sub>, then hydrazine was immediately added and the system was sealed. Blue-photocatalytic tests for the H<sub>2</sub> production were carried out using a water–hydrazine solution (40 mmol L<sup>-1</sup>) without CdS photocatalyst (Blue-photolysis).

The amount of H<sub>2</sub> produced was followed by using a gas chromatograph Shimadzu G-08 equipped with a thermal conductivity detector (TCD) and a Shincarbon packed column (2 m length, 1 mm ID and 25 mm OD), using N<sub>2</sub> as carrier gas.

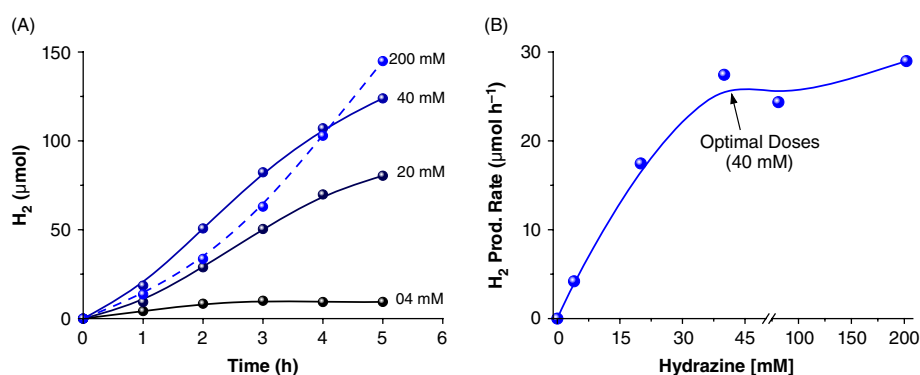
### •OH radical determination

Fluorescence spectra of 2-hydroxyterephthalic acid were measured on a SCINCO fluorescence spectrometer FS-2. The •OH radical generated with the CdS semiconductor under blue irradiation in the absence or presence of hydrazine (20 mmol L<sup>-1</sup>) was evaluated using the following procedure: terephthalic acid (TA, 5 × 10<sup>-4</sup> mol L<sup>-1</sup>) was dissolved in a water/NaOH solution (2 × 10<sup>-3</sup> mol L<sup>-1</sup>). Then, 20 mg of CdS powder was added and the suspension stirred for 30 min. Previous to the blue irradiation, the system was bubbled with N<sub>2</sub> to simulate the O<sub>2</sub>-free system; then the system was sealed and the blue LED lamp was turned on. Aliquots were taken every 10 min for 1 h per analysis. During the test, the system was set in the open air to simulate the oxidizing conditions (dissolved O<sub>2</sub>) and aliquots were also taken. The fluorescence emission spectra of the irradiated solution were analyzed by PL (excited at 320 nm) following the hydroxyterephthalic acid (HTA) formation at 425 nm.

## RESULTS AND DISCUSSION

### Characterization of CdS nanofibers

CdS has a morphology of flexible nanofibers (Fig. 1(A)) with a diameter (*D*) ranging from 10 to 15 nm and they are agglomerated forming a worsted-like structure. The length (*L*) is not possible to determine, but it can be seen that it is longer than 100 nm. The X-ray diffraction pattern (Fig. 1(B)) shows reflection peaks corresponding to the hexagonal structure of CdS according to the JCPDS card No. 41-1049, however, its lattice parameters (*a* = 0.404 and *c* = 0.66 nm) are smaller than those reported for the bulk CdS (*a* = 0.41 nm and *c* = 0.68 nm),<sup>21</sup> indicating that the hexagonal structure is slightly contracted, probably due to the presence of sulfur vacancies. The average crystallite size determined by the



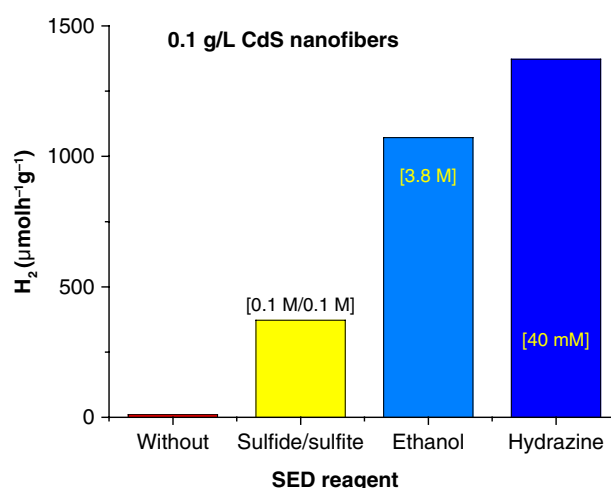
**Figure 2.** (A) Profile of H<sub>2</sub> evolution at different hydrazine doses as a function of time, and (B) profile of H<sub>2</sub> production rate as a function of hydrazine doses, with CdS nanofibers under blue irradiation.

Debye–Scherrer equation from the reflection peaks of the (002) plane is c. 6 nm. The diffuse reflectance spectrum (Fig. 1(C)) shows that the CdS nanofibers exhibit absorption edges from blue to UV regions from 490 to 200 nm. The intrinsic band-gap of the CdS nanofibers indicates that the electron transition from the valence band to the conduction band is blue-shifted in comparison with the bulk CdS, which is caused by the quantum size effect.<sup>27</sup> This optical absorption matches with the blue emission spectrum of the blue LED lamp used for its photonic activation (shaded area in Fig. 1(C)).

### H<sub>2</sub> evolution from water–hydrazine solution

The H<sub>2</sub> evolution profile from water contaminated with low hydrazine doses, 0.4 mmol L<sup>-1</sup>, (Fig. 2(A)) using a CdS photocatalyst produces a low amount of H<sub>2</sub>, where the H<sub>2</sub> evolution rate was linear only for 2 h, suggesting that the reaction was stopped after 2 h. With increasing hydrazine doses (20 or 40 mmol L<sup>-1</sup>), the H<sub>2</sub> evolution rate increased linearly in equal proportion for 4 h; later, a slight depletion was observed. The H<sub>2</sub> evolution rate as a function of hydrazine doses (Fig. 2(B)), indicates that the hydrazine doses (0.4–40 mmol L<sup>-1</sup>) linearly increase the H<sub>2</sub> evolution rate from 0.4 to 27 μmol h<sup>-1</sup>, and it remains unaltered at doses higher than 40 mmol L<sup>-1</sup>. The H<sub>2</sub> evolution rate from pure water (without hydrazine) was almost negligible (<1 μmol h<sup>-1</sup>), but with 40 mmol L<sup>-1</sup> of hydrazine, the H<sub>2</sub> evolution rate increased 27 times. The H<sub>2</sub> evolution from the water–hydrazine (40 mmol L<sup>-1</sup>) solution in the absence of photocatalyst was completely negligible, indicating that the CdS photocatalyst is required to produce H<sub>2</sub>. The rate of H<sub>2</sub> produced was standardized to μmol h<sup>-1</sup> g<sup>-1</sup>, considering the used powder load (20 mg of CdS). Thus, the intrinsic H<sub>2</sub> evolution rate from pure water is 10 μmol h<sup>-1</sup> g<sup>-1</sup> and from the water–hydrazine solution is 1372 μmol h<sup>-1</sup> g<sup>-1</sup> (Fig. 3), where 40 mmol L<sup>-1</sup> of hydrazine dose is the optimal value to reach the highest H<sub>2</sub> production.

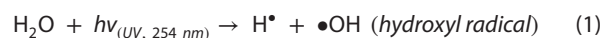
The intrinsic rate of CdS for the H<sub>2</sub> production from water–hydrazine solution was compared with the other SEDs reagents (Fig. 3). Poor H<sub>2</sub> evolution rate (372 μmol h<sup>-1</sup> g<sup>-1</sup>) was obtained with the sulfite/sulfide solution; meanwhile an evolution rate of 1072 μmol h<sup>-1</sup> g<sup>-1</sup> was obtained with a high ethanol concentration. These results suggest that the type and concentration of SEDs reagents determine the amount of generated H<sub>2</sub> by using CdS nanofibers. Considering that the doses of hydrazine hydrate in the aqueous solution are extremely low (<40 mmol L<sup>-1</sup>), the hydrazine contaminant can be valued as the best SEDs (*hole scavenger*), resulting in improvement of the efficiency of H<sub>2</sub> production.



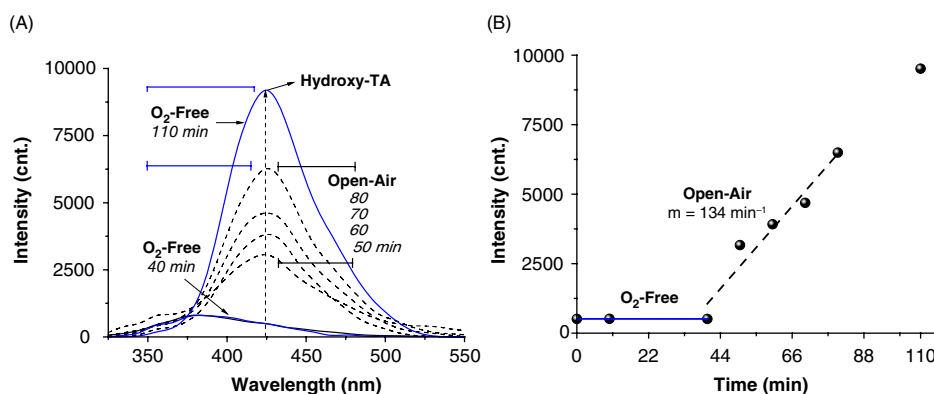
**Figure 3.** Comparison of H<sub>2</sub> evolution without and with different sacrificial electron donors (SED) by using CdS nanofiber under Blue-irradiation.

### •OH radical determination

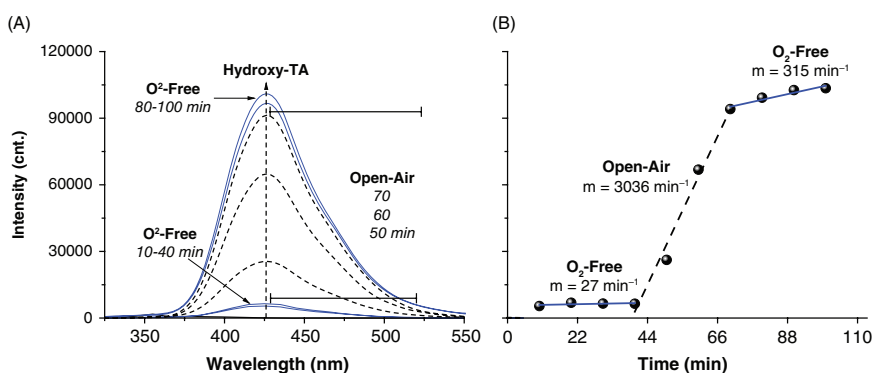
The •OH radical formation in the irradiated water with Blue light in either an O<sub>2</sub>-free system (O<sub>2</sub>-Free) bubbling with N<sub>2</sub> or oxidizing conditions (Open-Air) in an open-air system, was determined following the fluorescence signal at 425 nm of the formed hydroxyterephthalic acid (HTA).<sup>28</sup> It is known that when water is irradiated with high energy irradiation, the •OH radicals are formed (Equation (1)) and they can be trapped by the terephthalic acid (TA), forming HTA (Equation (2)), whereas the •H radical forms H<sub>2</sub> (Equation (3)) by the following equations:



However, under visible light, the •OH radicals from water are hardly formed. Thus, in our studies, when the terephthalic acid (TA) in aqueous solution was irradiated with blue-light in the absence of photocatalyst (Blue-photolysis) with either an O<sub>2</sub>-free system or open-air system, the fluorescence signal corresponding to HTA was not detected (not shown), indicating a negligible •OH radical formation from water. It can be explained by the fact that the blue-light is not energetic enough and, as a



**Figure 4.** (A) Fluorescence spectra of Hydroxy-TA, and (B) profile of the Hydroxy-TA formation rate as a function of time by using CdS nanofiber photocatalyst during the blue-irradiation.



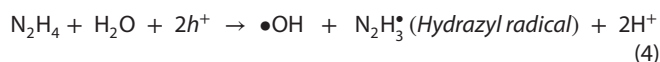
**Figure 5.** (A) Fluorescence spectra of Hydroxy-TA, and (B) profile of the Hydroxy-TA formation rate as a function of time by using CdS nanofiber in the presence of hydrazine during the blue-irradiation.

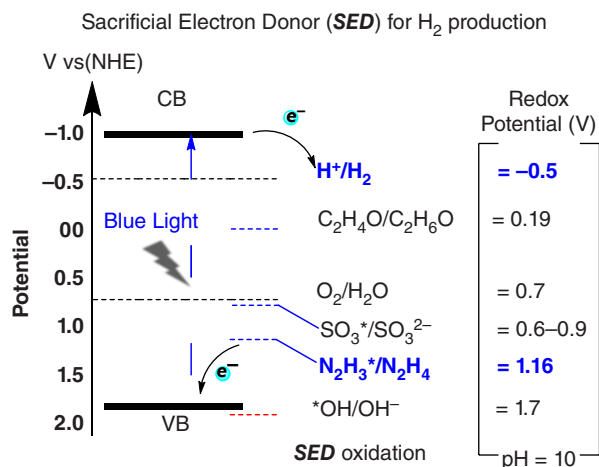
consequence, the blue-light cannot split water. By using a CdS photocatalyst, the  $\bullet\text{OH}$  radical formation was almost negligible with the  $\text{O}_2$ -free system ( $\text{O}_2$ -Free); by contrast, with the open-air system, HTA was detected (Fig. 4(A)), suggesting an  $\bullet\text{OH}$  radical formation rate of  $134 \text{ min}^{-1}$  (Fig. 4(B)). The negligible  $\bullet\text{OH}$  radical formation from water with the  $\text{O}_2$ -free system can explain the observed low  $\text{H}_2$  production rate ( $<1 \mu\text{mol h}^{-1}$ ), where the CdS photocatalyst is poorly active for water splitting in the absence of a SED.

The  $\bullet\text{OH}$  radical formation from water contaminated with hydrazine using CdS under blue-irradiation was also investigated in either  $\text{O}_2$ -free systems or open-air systems (Fig. 5(A)–(B)). In an  $\text{O}_2$ -free system, HTA was formed during the first 10 min, but after that, the fluorescence signal at 425 nm was unaltered as the irradiation time continued until 40 min (Fig. 5(A)), indicating the negligible formation of  $\bullet\text{OH}$  radicals. On the other hand, in an open-air system, the increasing HTA signal suggests that the  $\bullet\text{OH}$  radicals were increasingly formed, reaching a formation rate of  $3036 \text{ min}^{-1}$  (Fig. 5(B)), which is huge in comparison with that generated in pure water (Fig. 4(B)). These results suggest that the  $\bullet\text{OH}$  radicals do not participate in the mechanism of  $\text{H}_2$  evolution from the water–hydrazine solution in the  $\text{O}_2$ -free system and that hydrazine as SED is needed to achieve the release of  $\text{H}_2$  from water. On the other hand, in the open-air system, it can be expected that hydrazine can be photodecomposed by the holes photogenerated on the CdS surface and the formed intermediary products in the presence of dissolved  $\text{O}_2$  contribute to the generation of the large amount of  $\bullet\text{OH}$  radicals but without  $\text{H}_2$  evolution.

### Mechanism of $\text{H}_2$ production from water–hydrazine solution

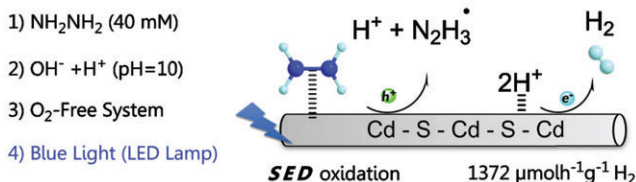
The nil  $\text{H}_2$  evolution from the Blue-photolysis of either water or water–hydrazine under blue-irradiation indicates that both water and the hydrazine molecule cannot be oxidized by the blue-light and therefore  $\text{H}_2$  generation (Equation (3)) cannot be achieved. However, when CdS is used, water as well as hydrazine are split and photodecomposed, respectively, by the positive holes photogenerated on the CdS surface, forming hydrazyl radicals and partially hydroxyl radical (Equation (4)), whereas the photogenerated electrons react with the protons ( $\text{H}^+$ ) to produce  $\text{H}_2$  (Equation (5)). The oxidation mechanism of hydrazine in aqueous solution involves several intermediaries that include hydroxylamines and ammonia until the formation of  $\text{N}_2$ .<sup>29</sup> According to the redox potential of the couple of each SED (Fig. 6), all of them can be oxidized by the blue-photogenerated holes formed in the positive valence band of the CdS nanofibers located at 1.6 V at pH = 10; however, the  $\bullet\text{OH}$  radical cannot be formed due to the high positive redox potential of  $\bullet\text{OH}/\text{HO}^- = 1.7 \text{ V}$ ,<sup>16</sup> whereas the redox potential of  $\text{N}_2\text{H}_3^\bullet/\text{N}_2\text{H}_4 = 1.16$  is low and therefore hydrazine can be photooxidized until the formation of tetrazane (Equation (6))<sup>30</sup> by the CdS holes, achieving  $\text{H}_2$  evolution by the electron–hole charge separation (Fig. 7).





**Figure 6.** Potential diagram for the photocatalytic H<sub>2</sub> production with feasible SED photooxidation over CdS as photocatalysts.

## Photodecomposition of Hydrazine-Aqueous



**Figure 7.** Mechanism of photodecomposition of hydrazine in aqueous solution by using CdS nanofibers under blue-irradiation.

## CONCLUSIONS

CdS under blue-irradiation can conduct the electron transfer process for the photocatalytic H<sub>2</sub> evolution by using different sacrificial electron donors in aqueous solution. The highest amount of H<sub>2</sub> produced was successfully achieved from water-hydrazine with hydrazine doses of 40 mmol L<sup>-1</sup> in an O<sub>2</sub>-free system. Small doses of hydrazine used as a 'hole scavenger' are better than huge concentrations of ethanol (3.8 mol L<sup>-1</sup>) in aqueous solution. The •OH radicals are not formed during the reaction and do not participate in the H<sub>2</sub> evolution mechanism from water-hydrazine in an O<sub>2</sub>-free system. Then, hydrazine is photodecomposed by the photogenerated holes during the blue-irradiation, whereas the H<sup>+</sup> ions are reduced by the electrons in the conduction band. This photocatalytic process using water contaminated with hydrazine could be an interesting alternative for the energy generation using solar light.

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