Photocatalytic Hydrogen Production: Role of Sacrificial Reagents on the Activity of Oxide, Carbon, and Sulfide Catalysts

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Abstract: Photocatalytic water splitting is a sustainable technology for the production of clean fuel in terms of hydrogen (H2). In the present study, hydrogen (H2) production efficiency of three promising photocatalysts (titania (TiO2-P25), graphitic carbon nitride (g-C3N4), and cadmium sulfide (CdS)) was evaluated in detail using various sacrificial agents. The effect of most commonly used sacrificial agents in the recent years, such as methanol, ethanol, isopropanol, ethylene glycol, glycerol, lactic acid, glucose, sodium sulfide, sodium sulfite, sodium sulfide/sodium sulfite mixture, and triethanolamine, were evaluated on TiO2-P25, g-C3N4, and CdS. H2 production experiments were carried out under simulated solar light irradiation in an immersion type photo-reactor. All the experiments were performed without any noble metal co-catalyst. Moreover, photolysis experiments were executed to study the H2 generation in the absence of a catalyst. The results were discussed specifically in terms of chemical reactions, pH of the reaction medium, hydroxyl groups, alpha hydrogen, and carbon chain length of sacrificial agents. The results revealed that glucose and glycerol are the most suitable sacrificial agents for an oxide photocatalyst. Triethanolamine is the ideal sacrificial agent for carbon and sulfide photocatalyst. A remarkable amount of H2 was produced from the photolysis of sodium sulfide and sodium sulfide/sodium sulfite mixture without any photocatalyst. The findings of this study would be highly beneficial for the selection of sacrificial agents for a particular photocatalyst.

Keywords: photocatalysis; TiO2; g-C3N4; CdS; energy

1. Introduction

Photocatalytic hydrogen (H2) production via water splitting is a sustainable and renewable energy production technology with negligible impact on the environment [1] (Figure 1). H2 is one of the most promising and clean energy sources for the future, with water as the only combustion product. After the invention of photo-electrochemical water splitting in 1972 [2] by Fujishima and Honda, nearly 9000 research articles have been published, outlining the use of various photocatalysts. In particular, most of the research works have been carried out using powder photocatalysts (except photo-electrochemical studies). The reported materials in the recent years are categorized as oxide
[3–149], carbon [3,81,150–237], and sulfide [3,14,17,25,58,59,113,114,119,128,133,154,164,169,177,181,195,203,208,210,215,220,227,230,235,238–345] photocatalysts. Titanium oxide–P25 (TiO$_2$-P25), graphitic carbon nitride (g-C$_3$N$_4$), and cadmium sulfide (CdS) are the most extensively studied photocatalysts for water splitting. Many review articles have also been published [1,116,163,167,225,237,238,245,346–419] discussing the various features of the photocatalytic water splitting, such as fundamental concepts, theoretical principles, nature (morphology, surface characteristics, and optical properties) of the photocatalyst, role of co-catalyst/sacrificial reagents, mechanism, kinetics, etc. Nevertheless, there is still not many comprehensive studies to identify an appropriate sacrificial reagent with respect to the nature of a photocatalyst.

Sacrificial agents or electron donors/hole scavengers play a prominent role in photocatalytic H$_2$ production because the water splitting is energetically an uphill reaction ($\Delta H^0 = 286$ kJ mol$^{-1}$). It is realized that methanol, triethanolamine, and sodium sulfide/sodium sulfite are the most commonly used sacrificial reagents for oxide, carbon, and sulfide photocatalysts, respectively. In most of the cases, fresh water (e.g., deionized water or double distilled water) has been used to evaluate the H$_2$ production efficiency in a micro photo-reactor (volume in the range of 30 to 70 mL) with a strong light irradiation source (nearly $\leq 300$ W). However, the vitality and utilization of this technology have not been comprehensively studied in a real environment. Moreover, the commercialization of this technology is still restrained by its poor efficiency and the use of expensive noble metals (like Pt, Au, Pd, Rh) as co-catalysts. Most of the published results do not have much consistency in terms of efficiency. For example, different efficiency values have been reported for pure TiO$_2$ using methanol as a scavenger (Table 1). This discrepancy is ascribed to the following reasons: photo-reactor design, inert gas (Ar or N$_2$) purging flow rate, light irradiation source, gas sampling method, gas chromatography (GC) analysis conditions, calculations, etc.
Table 1. Photocatalytic H₂ production efficiency of TiO₂ using methanol sacrificial agent.

<table>
<thead>
<tr>
<th>Catalyst Amount (g/L)</th>
<th>Concentration of Methanol (%)</th>
<th>Light Source</th>
<th>H₂ Production Efficiency (µmol/g/h)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>300 W of Xe (without UV cutoff filter)</td>
<td>42.00</td>
<td>[420]</td>
</tr>
<tr>
<td>0.6</td>
<td>16.66</td>
<td>300 W of Xe (with UV cutoff filter)</td>
<td>18.47</td>
<td>[217]</td>
</tr>
<tr>
<td>0.5</td>
<td>20</td>
<td>300 W of Xe (with UV cutoff filter)</td>
<td>~20.00</td>
<td>[194]</td>
</tr>
<tr>
<td>1.29</td>
<td>25.8</td>
<td>300 W of Xe (with UV cutoff filter)</td>
<td>~2.00</td>
<td>[421]</td>
</tr>
</tbody>
</table>

The photochemical reactions of sacrificial agents (methanol, ethanol, isopropanol, ethylene glycol, glycerol, glucose, lactic acid, triethanolamine, sodium sulfide, sodium sulfite, and sodium sulfide/sodium sulfite mixture) and their degradation products during H₂ production are summarized as follows:

**Methanol [422] (MeOH):**

\[
\begin{align*}
\text{H}_2\text{O}(l) + h^+ & \rightarrow *\text{OH} + \text{H}^+ & (1) \\
\text{CH}_3\text{OH}(l) + *\text{OH} & \rightarrow *\text{CH}_2\text{OH} + \text{H}_2\text{O}(l) & (2) \\
*\text{CH}_2\text{OH} & \rightarrow \text{HCHO}(l) + \text{H}^+ + e^- & (3) \\
2\text{H}^+ + 2e^- & \rightarrow \text{H}_2 & (4) \\
\text{HCHO}(l) + \text{H}_2\text{O}(l) & \rightarrow \text{HCOOH}(l) + \text{H}_2(g) & (5) \\
\text{HCOOH}(l) & \rightarrow \text{CO}_2(g) + \text{H}_2(g) & (6) \\
\end{align*}
\]

Overall reaction:

\[
\text{CH}_3\text{OH}(l) + \text{H}_2\text{O}(l) \rightarrow \text{CO}_2(g) + 3\text{H}_2(g) & (7)
\]

**Ethanol [423] (EtOH):**

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH} + \text{TiO}_2 & \rightarrow (s) \text{CH}_3\text{CH}_2\text{O} - \text{Ti}^{4+} + (s) \text{OH} & (8) \\
\text{TiO}_2 + \text{UV light} & \rightarrow 2e_{(a)}^- + 2h^+ & (9) \\
(s) \text{CH}_3\text{CH}_2\text{O} - \text{Ti}^{4+} + 2h^+ & \rightarrow (s) \text{CH}_3\text{CHO} + \text{Ti}^{4+} & (10) \\
(s) 2\text{OH} + e_{(a)}^- & \rightarrow \text{H}_2 + (s) 2\text{O}^{2+} & (11) \\
\end{align*}
\]

Here, (s) represents the photocatalyst surface and (a) denotes the photo-excited electrons by UV light.

**Isopropanol [424] (IPA):**

\[
\begin{align*}
\left[\text{S}_{\text{Cd}^{2+}}^{2-} > \text{(CdS)}\right]_2 + \text{H}_2\text{O} & \rightarrow \text{S}_{\text{Cd}^{2+}}^{2-} > \text{Cd(II)SH} + \text{S}_{\text{Cd}^{2+}}^{2-} > \text{S}(-\text{II})\text{Cd(II)OH} & (12) \\
\text{S}_{\text{Cd}^{2+}}^{2-} > \text{CdSH}_2^{2+} & \rightarrow \text{S}_{\text{Cd}^{2+}}^{2-} > \text{CdSH} + \text{H}^+ & (13) \\
\text{S}_{\text{Cd}^{2+}}^{2-} > \text{CdSH} & \rightarrow \text{S}_{\text{Cd}^{2+}}^{2-} > \text{CdS}^- + \text{H}^+ & (14) \\
\text{S}_{\text{Cd}^{2+}}^{2-} > \text{CdOH}_2^{2+} & \rightarrow \text{S}_{\text{Cd}^{2+}}^{2-} > \text{CdOH} + \text{H}^+ & (15) \\
\text{S}_{\text{Cd}^{2+}}^{2-} > \text{CdOH} & \rightarrow \text{S}_{\text{Cd}^{2+}}^{2-} > \text{CdO}^- + \text{H}^+ & (16) \\
\end{align*}
\]
\[ S^2_{\text{Cd}^{2+}} > \text{Cd}(\text{II})S(\text{I})^+ + \text{C}_3\text{H}_2\text{OH} \rightarrow S^2_{\text{Cd}^{2+}} > \text{Cd}(\text{II})S(\text{I})\text{H}^+ + \text{C}_3\text{H}_6\text{OH} \]  
(17)

\[ S^{2-}_{\text{Cd}^{2+}} > \text{Cd}(\text{II})S(\text{I})\text{H}^+ + \text{C}_3\text{H}_2\text{OH} \rightarrow S^{2-}_{\text{Cd}^{2+}} > \text{Cd}(\text{II})S(\text{I})\text{H}_2^+ + \text{C}_3\text{H}_6\text{OH} \]  
(18)

\[ 2\text{H}^+ \rightarrow \text{H}_2 \]  
(19)

\[ 2\text{C}_3\text{H}_6\text{OH} \rightarrow 2\text{C}_3\text{H}_5\text{O} + \text{H}_2 \]  
(20)

\[ S^2_{\text{Cd}^{2+}} > \text{Cd}(\text{II})S(\text{I})\text{H}_2^+ \rightarrow S^2_{\text{Cd}^{2+}} > \text{Cd}(\text{II})S(\text{I})\text{H}^+ + \text{H}^+ \]  
(21)

\[ S^{2-}_{\text{Cd}^{2+}} > \text{CdOH} + e^-_{\text{CB}} \rightarrow S^{2-}_{\text{Cd}^{2+}} > \text{CdO}^- + \text{H}^+ \]  
(22)

**Ethylene Glycol [76,425] (EG):**

\[
\text{OHCH}_2 - \text{CH}_2\text{OH} + \text{H}_2\text{O} \xrightarrow{\text{TiO}_2, \text{hv}} \text{OHCH}_2 - \text{CHO} \\
\text{OHCH}_2 - \text{CHO} + \text{OH} \rightarrow \text{OHCH}_2 - \text{COOH} \\
\text{OHCH}_2 - \text{COOH} \rightarrow \text{CH}_3\text{COOH} \\
\text{OHCH}_2 - \text{COOH} \rightarrow \text{HOOC} - \text{COOH} \\
\text{HOOC} - \text{COOH} \rightarrow \text{HCOOH} \\
\text{HCOOH} \text{ (or) } \text{CH}_3\text{COOH} \text{ (or) } \text{HOOC} - \text{COOH} \rightarrow \text{CO}_2 + \text{H}_2 + \text{CH}_4 + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 + \text{H}_2\text{O} 
\]  
(23-28)

**Glycerol [130] (GLY):**

\[
\text{C}_3\text{H}_6\text{O}_3 + 3\text{H}_2\text{O} + 14\text{h}^+_{\text{VB}} \rightarrow \text{intermediates} \ (\text{C}_4\text{H}_4\text{O}_2, \text{C}_2\text{H}_2\text{O}_2, \text{C}_2\text{H}_4\text{O}_3, \text{C}_3\text{H}_6\text{O}_3, \text{etc}) \\
\rightarrow 3\text{CO}_2 + 14\text{H}^+ \\
14\text{H}^+ + 14e^-_{\text{CB}} \rightarrow 7\text{H}_2 \ (g) 
\]  
(29-30)

**Glucose [9] (GLU):**

\[
\text{C}_6\text{H}_12\text{O}_6 + \text{H}_2\text{O} \text{ (anaerobic)} \rightarrow \text{C}_3\text{H}_10\text{O}_5 + \text{HCOOH} + \text{H}_2\ (g) 
\]  
(31)

\[
\text{C}_5\text{H}_10\text{O}_5 + \text{H}_2\text{O} \rightarrow \text{C}_4\text{H}_8\text{O}_4 + \text{HCOOH} + \text{H}_2\ (g) 
\]  
(32)

\[
\text{C}_4\text{H}_8\text{O}_4 + \text{H}_2\text{O} + \text{HCOOH} + \text{H}_2\ (g) \text{ (aerobic)} \rightarrow \text{HCOOH} + \text{H}_2\ (g) + \text{CO}_2\ (g) 
\]  
(33)

\[
\text{C}_6\text{H}_12\text{O}_6 \xrightarrow{\text{TiO}_2, \text{hv},\text{H}_2\text{O},\text{O}_2} \text{C}_6\text{H}_12\text{O}_7 
\]  
(34)

\[
\text{C}_6\text{H}_12\text{O}_7 \xrightarrow{\text{TiO}_2, \text{hv},\text{H}_2\text{O},\text{O}_2} \text{C}_6\text{H}_10\text{O}_8 
\]  
(35)

\[
\text{C}_6\text{H}_10\text{O}_8 \xrightarrow{\text{TiO}_2, \text{hv},\text{H}_2\text{O},\text{O}_2} \text{HCOOH} + \text{H}_2\ (g) + \text{CO}_2\ (g) 
\]  
(36)

**Lactic Acid [426] (LA):**

\[
\text{CH}_3 - \text{CH(OH)} - \text{COOH} + \text{H}_2\text{O} \xrightarrow{\text{TiO}_2, \text{hv}} \text{CO}_2 + \text{H}_2 + \text{CH}_3 - \text{CO} - \text{COOH} 
\]  
(37)

**Triethanolamine [427] (TEOA):**

\[
\text{C}_6\text{H}_15\text{NO}_3 \rightarrow \text{C}_6\text{H}_15\text{NO}_3^+ + e^- 
\]  
(38)

\[
\text{C}_6\text{H}_15\text{NO}_3^+ \rightarrow \text{C}_6\text{H}_14\text{NO}_3^+ + \text{H}^+ 
\]  
(39)

\[
\text{C}_6\text{H}_14\text{NO}_3^+ \rightarrow \text{C}_6\text{H}_14\text{NO}_3^+ + e^- 
\]  
(40)
\[
C_8H_{14}NO_3^+ + H_2O \rightarrow C_4H_{11}NO_3 + CH_3CHO + H^+ \quad (41)
\]

**Sodium sulfide (Na\textsubscript{2}S) [428]:**

\[
Na_2S + H_2O \rightarrow 2Na^+ + S^{2-} \quad (42)
\]

\[
S^{2-} + H_2O \rightarrow HS^- + OH^- \quad (43)
\]

\[
HS^- + hv \rightarrow HS^- \quad (44)
\]

\[
HS^- + HS^- \rightarrow [(HS)_2]^{2-} \rightarrow H_2 + S_2^{2-} \quad (45)
\]

**Sodium sulfite (Na\textsubscript{2}SO\textsubscript{3}) [429]:**

Irradiation:

\[
\text{SO}_3^{2-} \xrightarrow{hv} \text{SO}_2^{2-} \quad (46)
\]

Oxidation:

\[
\text{SO}_2^{2-} + 2OH^- \rightarrow \text{SO}_4^{2-} + H_2O + 2e^- \quad (47)
\]

Reduction:

\[
2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (48)
\]

Oxidation:

\[
2\text{SO}_3^{2-} \rightarrow \text{S}_2\text{O}_5^{2-} + 2e^- \quad (49)
\]

Reduction:

\[
2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (50)
\]

**Sodium sulfide and sodium sulfite mixture (Na\textsubscript{2}S and Na\textsubscript{2}SO\textsubscript{3}) [430]:**

Two different reaction pathways are involved when sodium sulfide and sodium sulfite mixture is used as a sacrificial agent.

\[
\text{HS}^-_{(aq)} \rightarrow \text{HS}^-_{(ads)} \quad (51)
\]

\[
\text{HS}^-_{(ads)} \xrightarrow{hv} [\text{HS}^-_{(ads)}]^+ \quad (52)
\]

**Path A:**

\[
[\text{HS}^-_{(ads)}]^+ \rightarrow H^+ + S^-_{(ads)} \quad (53)
\]

\[
\text{S}^-_{(ads)} + [\text{HS}^-_{(ads)}]^+ \rightarrow [\text{HS}_2^2]^- \quad (54)
\]

\[
[\text{HS}_2^2]^- \varphi \rightarrow H^+ + S_2^{2-} \quad (55)
\]

\[
2H^+ \rightarrow H_2 \quad (56)
\]

**Path B:**

\[
[\text{HS}^-_{(ads)}]^+ + S^0_{(ads)} \rightarrow [\text{HS}_2^-] \varphi \quad (57)
\]

\[
[\text{HS}_2^-] \varphi + \text{OH}^- + \text{SO}_3^{2-} + S^0_{(ads)} \rightarrow [\text{HS}_2^2]^- \varphi + \text{OH}^+ + \text{S}_2\text{O}_5^{2-} \quad (58)
\]

\[
\text{OH}^+ + \text{SO}_3^{2-} \xrightarrow{hv} \text{SO}_4^{2-} + H^+ \quad (59)
\]

\[
2H^+ \rightarrow H_2 \quad (60)
\]

\[
[\text{HS}^-_{(ads)}]^+ + \text{H}_2\text{O} \rightarrow S^0_{(ads)} + \text{H}_2 + \text{OH}^- \quad (61)
\]

\[
[\text{HS}_2^-] \varphi + \text{OH}^- \rightarrow \text{H}_2\text{O} + S_2^{2-} \quad (62)
\]

where (ads) denotes adsorption and \( \varphi \) represents species, which can undergo intramolecular charge transfer.

The previous articles reported \( \text{H}_2 \) production efficiencies with various combinations of photocatalysts and sacrificial reagents. This study provides detailed information on the selection of sacrificial reagents and photocatalysts for \( \text{H}_2 \) production. The efficiencies of \( \text{TiO}_2 - \text{P}25, \text{g-C}_3\text{N}_4 \), and \( \text{CdS} \) were evaluated using methanol (MeOH), ethanol (EtOH), isopropanol (IPA), ethylene glycol
(EG), glycerol (GLY), lactic acid (LA), glucose (GLU), sodium sulfide (Na$_2$S), sodium sulfite (Na$_2$SO$_3$), sodium sulfide/sodium sulfite mixture (Na$_2$S/Na$_2$SO$_3$), and triethanolamine (TEOA) as sacrificial reagents (organic and inorganic). The efficiency of a photocatalyst was described in terms of pH of medium and nature of the sacrificial agent (carbon chain length, alpha hydrogen, hydroxyl groups, binding interactions, etc). Besides, control experiments were executed to investigate the H$_2$ production with only sacrificial reagents under solar light irradiation in the absence of photocatalyst.

2. Results and Discussion

2.1. TiO$_2$ P25

Figure 2 shows the H$_2$ production efficiency of TiO$_2$ P25 using various sacrificial agents. H$_2$ production efficiencies of TiO$_2$/EG, TiO$_2$/GLY, TiO$_2$/Na$_2$S/Na$_2$SO$_3$, TiO$_2$/GLU, TiO$_2$/Na$_2$S were found to be 190.2 µmol, 130.8 µmol, 126 µmol, 120 µmol, and 120 µmol, respectively. H$_2$ production efficiency of TiO$_2$/MeOH system reduced to 81.6 µmol for the same period. The use of TEOA, EtOH, IPA, and Na$_2$SO$_3$ as sacrificial reagents resulted in poor H$_2$ production, yielding 61.8 µmol, 49.8 µmol, 46.2 µmol, and 40.8 µmol, respectively. TiO$_2$/LA mixture displayed the lowest yield of H$_2$ production (only 27.6 µmol). TiO$_2$/EG mixture showed the maximum H$_2$ production (190.2 µmol) efficiency as compared to all other combinations. This is ascribed to the faster charge transfer reaction in the TiO$_2$/EG system compared to the photo-generated electron-hole recombination process [431,432].

The length of the carbon chain, the number of hydroxyl groups, and dehydrogenation/decarbonylation characteristics of sacrificial agents are the primary features in controlling the H$_2$ production efficiency. Moreover, the following properties of sacrificial agents could also strongly influence the efficiency: polarity and electron donating ability, adsorption capability on the photocatalyst surface, the formation of by-products, and the selectivity for reaction with photo-generated holes (e.g., decarboxylation process) [10,94,431–436]. Carbon monoxide (CO) is one of the main intermediates for the alcohols with a short carbon chain. Hence, the adsorption of CO on the active sites of TiO$_2$ via chemisorption restricts further adsorption of alcohol on the photocatalyst surface [437]. The removal of CO as CO$_2$ is the rate-determining step in H$_2$ production. It depends on the adsorption efficiency and the number of alpha hydrogens of the sacrificial agent [437]. During the water-splitting process, the hydroxyl radical (•OH) abstracts alpha hydrogen from the alcohol to create •RCH$_2$-OH radical, which gets further oxidized into an aldehyde, carboxylic acid, and CO$_2$ [437]. Bahruji et al. [437] suggested that alkyl groups connected to the alcohol (e.g., C$_x$H$_y$OH) could yield the respective alkanes (e.g., C$_{x-1}$) during the water-splitting process. The alkane production rate was decreased with the increase of OH groups in alcohol [438]. In the case of polyols, the hydrogen atoms from the alpha carbon could be easily extracted and evolved in the form of H$_2$ [438]. The alpha carbon atoms could be oxidized into CO$_2$. The C atoms without OH groups (other than alpha C atoms) would be evolved in the form of alkanes [438].

Time-resolved transient absorption spectroscopy results revealed that carbohydrates and polyols (C$_2$–C$_6$) could rapidly react with ~50–60% holes (h$^+$) within 6 ns as compared to other alcohols [439,440]. The OH groups could act as an anchor for the chemisorption of alcohols on the photocatalyst surface [438]. The coordination efficiency of alcohols with the Ti sites relies on the number of OH groups and the carbon chain length. This type of linkage could be beneficial for the utilization of holes to improve the H$_2$ production and suppress the charge carrier recombination [438].

The first principle calculations showed that the formation of gap levels in TiO$_2$ via the adsorption polyols could accelerate the hole trapping process [441]. Though EG showed maximum efficiency for TiO$_2$-P25, glycerol and glucose are the most appropriate sacrificial agents for any kind of oxide photocatalyst. This owes to their (glucose and glycol) most abundance, less toxicity, low cost, and they can readily undergo dehydrogenation as compared to other alcohols [40,63,435].
2.2. g-C₃N₄

H₂ production efficiency of g-C₃N₄ with various sacrificial agents is shown in Figure 3. In this case, only the use of TEOA, Na₂S, Na₂SO₃, and Na₂S/Na₂SO₃ resulted in H₂ production. H₂ production efficiency of g-C₃N₄/Na₂S (139.8 µmol) system was higher than that of g-C₃N₄/Na₂S/Na₂SO₃ (127.2 µmol) and g-C₃N₄/Na₂SO₃ (5.4 µmol). g-C₃N₄/TEOA mixture showed the best efficiency (247.2 µmol) when compared to all other sacrificial agents. This can be ascribed to the fact that photo-corrosion and degradation of π conjugated structure [304] of amine rich g-C₃N₄ is secured by the effective binding of TEOA on the catalyst surface [112]. TEOA excellently consumes the photo-generated holes, improves the dispersion of photocatalyst, and acts as a binding ligand to improve the interaction of g-C₃N₄ with water molecules [204,442]. The results shown in Figure 3 also suggest that alcohols and glucose are not strongly adsorbed on the g-C₃N₄ surface for water-splitting reaction. This is attributed to the absence of hydrophilicity and surface characteristics (e.g., active sites, poor electrical conductivity, water oxidation ability) of g-C₃N₄ to facilitate a strong interfacial electron/hole transfer process on the catalyst surface. The poor crystallinity and basal planar structure of g-C₃N₄ endorse the electron-hole recombination [443]. Moreover, high activation energy and overpotential are required for H₂ production on the g-C₃N₄ surface [182,211]. This could be rectified by the loading of noble metals or co-catalysts over g-C₃N₄ or fabricating Z-scheme photocatalysts. In most of the studies, it was reported that g-C₃N₄ acts as an outstanding template and there was no H₂ production on g-C₃N₄ without any noble metal co-catalyst [444,445]. The results also demonstrated that the light absorption capability, chemical stability, and suitable band edge positions of narrow band-gap g-C₃N₄ are not the only decisive factors to enhance the H₂ production efficiency.

Figure 2. Photocatalytic H₂ production efficiency of TiO₂-p25 using various sacrificial agents.
The electron-hole recombination process is strongly restrained by the sulfide ions at alkaline pH. When CdS is suspended in a water medium, thiol (Cd-SH) and hydroxyl (Cd-OH) groups are developed on its surface, which are highly pH dependent [310]. In the case of Na₂S, the pH of the medium is alkaline, sulfide (S₂⁻) and hydrogen sulfide (HS⁻) are formed when Na₂S is dissolved in water [310]. During light irradiation, S₂⁻ and HS⁻ are quickly oxidized into sulfate (SO₄²⁻) and polysulfide (S₄²⁻, S₅²⁻) ions, respectively [310]. The oxidation of sulfide by the photo-generated holes is much preferential as compared to the photo-corrosion of CdS [112]. The precipitation of yellow colored polysulfide ions diminishes the photocatalytic efficiency via acting as an optical filter and competing with sacrificial agents on the CdS surface.

2.3. CdS

Photocatalytic H₂ production efficiency of CdS using various sacrificial agents is shown in Figure 4. The use of TEOA, Na₂S, Na₂SO₃, Na₂S/Na₂SO₃, and LA as sacrificial reagents resulted in H₂ formation. CdS/TEOA system showed the maximum efficiency of 283.2 µmol of H₂ as compared to all other sacrificial agents. The efficiency of CdS/Na₂S, CdS/Na₂SO₃, CdS/LA systems was found to be 181.2 µmol, 154.8 µmol, and 84 µmol, respectively. The mixture of CdS/Na₂S/Na₂SO₃ showed the lowest H₂ production of 54 µmol after 6 h. Bare CdS is not stable under prolonged light irradiation because the sulfide ions on its surface are rapidly oxidized into sulfur through the reaction with photo-generated holes (photo-corrosion – CdS + 2h⁺ → Cd²⁺ + S) [308,446,447]. The sulfide oxidation of CdS can occur before the oxidation of water by holes [308,447]. Hence, the H₂ production efficiency of CdS highly relies on the effective binding of sacrificial agents on its surface. The results showed that amine and sulfide/sulfite might be strongly bound to the CdS surface and it could effectively consume the holes as compared to alcohol and sugars. It is obviously noted that H₂ is produced in high alkaline (amine, sulfide, and sulfite) and acidic (LA) pH mixtures when compared to neutral pH (alcohols and sugar). LA is converted into pyruvic acid and CO₂ during the water-splitting reaction; this may slightly influence the pH and polarity of the reaction mixture. The sulfide ions from Na₂S stabilizes CdS surface to terminate the surface defects originated from photo-corrosion. The electron-hole recombination process is strongly restrained by the sulfide ions at alkaline pH.

![Figure 3. Photocatalytic H₂ production efficiency of g-C₃N₄ using various sacrificial agents.](image-url)
with the H₂ generation reaction. This could be restricted by the addition of Na₂SO₃ to generate more HS⁻ and S₂O₃²⁻ ions to enhance the photocatalytic activity [292]. However, the results shown in Figure 4 suggest that H₂ production efficiency of Na₂S/CdS or CdS/Na₂SO₃ are higher than that of CdS/Na₂S/Na₂SO₃. The reasons could be predicted by the photolysis experiments of sacrificial agents. The pH of TEOA/water mixture would be around 12, which could enhance the H₂ production efficiency via strong interfacial bonding on the CdS surface and its reaction with photo-generated holes [204].

![Figure 4. Photocatalytic H₂ production efficiency of CdS using various sacrificial agents.](image)

### 2.4. Photolysis

Photolysis experiments were carried out for all sacrificial agents in water for 6 h of light irradiation without the additions of photocatalysts. Control experiments were also carried out in the absence of sacrificial agents to evaluate the efficiency of the photocatalyst. There was no H₂ production in the absence of any sacrificial agents for TiO₂-p25, g-C₃N₄, and CdS. The results of photolysis experiments with sacrificial reagents under solar light in the absence of photocatalysts are shown in Figure 5. Interestingly, a remarkable amount of H₂ was evolved from Na₂S/water (159 µmol), Na₂SO₃/water (51 µmol), and Na₂S/Na₂SO₃/water (134.4 µmol) systems without photocatalyst. It was observed that the H₂ production efficiency was increased with respect to the concentration of sulfide or sulfite. When compared to results obtained in the presence of photocatalysts, it could be observed that the photocatalysts, such as TiO₂-p25 and g-C₃N₄, surprisingly reduced the actual H₂ production efficiency of sulfide system. There was not a significant increment in the efficiency of CdS/Na₂S as compared to the photolysis of Na₂S. However, the efficiency of CdS/Na₂SO₃ was higher than that of Na₂SO₃ photolysis. It is also noted that a high concentration of sulfide/sulfite mixture (in the range of 0.2 M to 1 M) was used in most of the studies for H₂ production [246,264,273,300,448–451]. In such cases, the photolysis of sulfide or sulfite solutions were not evaluated. Hence, the H₂ production should have been mainly originated via photolysis of sulfide/sulfite mixture rather than the photocatalytic
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degradation of organic sacrificial agents in the solutions at the end of 6 h experiment. Table 2

2.5. TOC Analysis

tannery sludge wastewater for photocatalytic H2 generation using CdS. The photolysis of sulfide-rich

concentration of sacrificial agents was used to evaluate the photocatalytic activity. The photocatalytic

experiments were not described in detail. Moreover, the effect of most earth abundant glucose and

glycerol were not investigated on the H2 production efficiency. Sulfur dioxide (SO2) emission from

originated from HS– is efficiently consumed by SO32− to improve the photonic efficiency. It is strongly recommended to study the effect of photolysis when the sulfide/sulfite mixture is used as the sacrificial agent to evaluate the H2 production efficiency of the photocatalyst. The elemental sulfur could be filtered out by passing hydrogen sulfide (H2S) gas in the aqueous solution under nitrogen atmosphere [428]. The resulting filtrate could be reused for photolytic H2 production [428].

Li et al. [430] investigated the photochemical generation of H2 from sulfide and sulfite mixture solutions. They found that the pH of sulfide/sulfite mixture (~13.14) was slightly decreased (~12.94) after the completion of photolysis experiments. The addition of a small amount of sulfite into the sulfide solution could not amplify the H2 production. Nevertheless, the elemental sulfur or polysulfide originated from HS− is efficiently consumed by SO32− to improve the photonic efficiency. It is strongly recommended to study the effect of photolysis when the sulfide/sulfite mixture is used as the sacrificial agent to evaluate the H2 production efficiency of the photocatalyst. The elemental sulfur could be filtered out by passing hydrogen sulfide (H2S) gas in the aqueous solution under nitrogen atmosphere [428]. The resulting filtrate could be reused for photolytic H2 production [428].

Wang et al. [112] suggested that Na2S/Na2SO3, MeOH, and TEOA were the most appropriate sacrificial agents for sulfide, oxide, and carbon-based photocatalysts. However, the experiments were not performed to study the effect of photolysis, especially the sulfide or sulfite solutions. A high concentration of sacrificial agents was used to evaluate the photocatalytic activity. The photocatalytic experiments were not described in detail. Moreover, the effect of most earth abundant glucose and glycerol were not investigated on the H2 production efficiency. Sulfur dioxide (SO2) emission from the flue gas can be absorbed as Na2SO3 solution using dilute sodium hydroxide. The photolysis of such sodium sulfite solution is an eco-friendly way to produce H2 gas [429]. Only a few studies were focused on using wastewater for H2 generation. Souza and Silva [310] studied the feasibility of using tannery sludge wastewater for photocatalytic H2 generation using CdS. The photolysis of sulfide-rich wastewater or industrial effluent is the foremost choice to produce green energy in a sustainable way via photocatalysis.

2.5. TOC Analysis

TOC analysis was carried out for solutions after the photocatalytic experiments, to assess the degradation of organic sacrificial agents in the solutions at the end of 6 h experiment. Table 2
summarizes the TOC results for the solutions of TiO$_2$-p25. The results suggest the effective utilization of the organic sacrificial agents by TiO$_2$-P25 for H$_2$ production. TOC was reduced almost half for most of the sacrificial agents after 6 h except for glucose. This is ascribed to the formation of more organic intermediates when glucose is utilized as the sacrificial agent.

| Table 2. TOC of solutions after the completion of the photocatalytic reaction. |
|-----------------|-----------------|-----------------|
| Sample          | TOC (mg/L)      |                  |
|                 | Blank (Before Light Irradiation) | TiO$_2$-P25     |
| Water           | 8.659           | -               |
| Methanol        | 30,450          | 15,530          |
| Ethanol         | 43,680          | 17,070          |
| Isopropanol     | 55,010          | 17,770          |
| Glycerol        | 54,220          | 18,700          |
| Ethylene glycol | 59,080          | 17,930          |
| Glucose         | 7699            | 11,500          |
| Lactic acid     | 47,310          | 20,440          |

3. Experimental

All the chemicals used were of analytical grade and used as received without further purification. TiO$_2$ P25 was purchased from Sigma Aldrich (Darmstadt, Germany), g-CN$_3$N$_4$ was synthesized by the calcination of urea at 550 °C for 2 h [452]. CdS was synthesized via the hydrothermal method [453]. Photocatalytic experiments were carried out using an immersion type reactor (Lelesil innovative systems, Thane, Maharashtra, India) as shown in Figure 6. All the reactions were carried out without any noble metal co-catalyst. The reactor is a tightly closed setup with a total volume of 1000 mL. Reactions were carried out using 500 mL of double distilled water with 0.5 g/L of photocatalyst and desired amount of sacrificial reagent (based on the literature). The empty headspace was kept constant at 500 mL for all reactions. The sacrificial agent concentration was fixed at 10% (alcohol, amine, acid) and 0.1 M (glucose, sodium sulfide, sodium sulfite, sodium sulfide/sodium sulfite mixture). The mixture was stirred under nitrogen purging for 1 h after which, the purging was stopped, and the reactor was closed immediately. The mixture was irradiated using a 300 W Xenon arc lamp without any UV cutoff filter (simulated solar light source). H$_2$ sampling was carried out for every 1 h using a 250 µL sample lock gas tight syringe. At the end of the photoreaction time, when organic sacrificial reagents were used, the mixture was filtered using a 0.45 µm micro-filter, and the filtrate was analyzed using a total organic carbon (TOC; Shimadzu, Japan) analyzer to measure the loss of reagents by mineralization. H$_2$ was analyzed using Agilent gas chromatography (USA) with thermal conductivity detector (TCD), manual injection, carrier gas N$_2$, molecular sieve 5 Å column with 2-m length, front inlet temperature 140 °C, and detector temperature 150 °C.
Different types of photocatalysts have been successfully investigated for H\textsubscript{2} production using various organic and inorganic sacrificial agents. The surface of an oxide photocatalyst would be more suitable for polyls and sugars for adsorption as compared to amines and sulfides. Amines are the most appropriate of sacrificial agents for carbon and sulfide photocatalysts. CdS/TEOA (283.2 µmol), g-C\textsubscript{3}N\textsubscript{4}/TEOA (247.2 µmol), and TiO\textsubscript{2}/EG (190.2 µmol) are the three best systems with maximum H\textsubscript{2} production in this study. H\textsubscript{2} could also be generated via the direct photolysis of sodium sulfide solution in the absence of any catalyst. TiO\textsubscript{2}-p25 and g-C\textsubscript{3}N\textsubscript{4} suppress the self-H\textsubscript{2} generation efficiency of Na\textsubscript{2}S photolysis. More technological developments are required for the practical application of water-splitting in a scalable and economically feasible way. Stable, affordable, and active co-catalysts should be developed in the future to replace the expensive noble metals to achieve a significant amount of H\textsubscript{2} production. In most of the studies, precious fresh water with a high concentration of sacrificial agents was used in a small reactor to generate H\textsubscript{2}. Hence, future studies should be focused on a pilot scale using industrial wastewater and seawater rather than using fresh water.

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