Solar photocatalytic hydrogen production from glycerol reforming using ternary Cu/THS/Graphene

T W P Seadira1*, S J Baloyi1, C M Masuku2,3, M S Scurrell2

1 Advanced Materials Division, Catalysis Group, Mintek, Private Bag X3015, Randburg, 2125, South Africa.

2 Department of Civil and Chemical Engineering, University of South Africa, Private Bag X6, FLORIDA, 1710, South Africa.

3 Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA.

E-mail: tumelo.seadira@gmail.com

Abstract. A ternary Cu/THS/rGO photocatalyst was prepared using solvothermal method. Firstly, pure anatase TiO2 hollow spheres (THS) were prepared via hydrothermal method using titanium butoxide, ethanol, ammonium sulphate, and urea via hydrothermal method. The copper (Cu) nanoparticles were subsequently loaded on the surface of the THS by wet impregnation. During the solvothermal process, the deposition and well dispersion of Cu/THS composites onto the graphene oxide surface. Subsequently, the reduction of graphene oxide to graphene was achieved. The morphological and structural properties of the prepared samples were characterized by Scanning Electron Microscope (SEM), UV-vis DRS, and photoluminescence (PL). The activities of the prepared catalysts were tested for hydrogen production via simultaneous photocatalytic water-splitting and glycerol reforming under visible light irradiation. The excellent photocatalytic activity of the Cu/THS/rGO catalyst was attributed the rGO which acts as both storage and transferor of electrons generated at the Cu and TiO2 heterojunction, thus increasing the electro-hole pairs separation. Furthermore, the effects of reaction parameters photocatalytic hydrogen production were also studied.

1. Introduction

Photocatalysis has attracted a lot of attention as an alternative green and cost effective process for the production of clean-energy-source-hydrogen compared to the traditional high-energy-consuming processes such as steam reforming using fossil fuels, which leave a huge carbon footprint in the ecosystem [1]; [2]; [3]. However, the challenges associated with photocatalysis are the thermodynamic uphill of water splitting for hydrogen production, which results in low efficiency of hydrogen evolution [4]; and the development of highly active photocatalysts under solar irradiation [5]. It has been reported extensively that the thermodynamic uphill challenge can be addressed by the addition of sacrificial agents that are biomass derived feedstocks, that can be reformed easily and also act as the hole (h+) scavengers of the semiconductor photocatalysts during photocatalysis; therefore, increasing the hydrogen evolution efficiency [6]; [7]; [8]. Among the number of biomass derived feedstocks studied for photocatalytic hydrogen evolution, many authors reported that methane provided the highest rates of hydrogen. However, due to the industrial demand which drives up the cost of methane, makes it an unideal sacrificial agent for low cost hydrogen production [9]. Therefore, given is production in large amounts as a by-product of the biodiesel industry, glycerol has been identified as an alternative...
sacrificial agent because of its low cost and abundance. Furthermore, the processing of glycerol can relieve the cost of growing storage attached to it [10]; [11].

It is widely reported that the TiO$_2$ based materials impregnated with various metal particles such as Pt [12], Au [13], Pd [14], Ni [15], Ag [16], and Cu [17] are impressively active for hydrogen production from the photocatalytic reforming of glycerol. However, most precious metals such as Pt, Pd, Au, are costly, and therefore limiting their utilization as co-catalysts. Therefore, research had been focused on developing nano-structured TiO$_2$ materials such as nanotubes [16], nanoflowers [18], and nano-hollow-spheres [18], in order to enhance the photocatalytic activity for hydrogen production using transition metals which are less costly. Furthermore, it has been reported that the incorporation of graphene sheets to these co-catalysts will further increase their photocatalytic activity [19]; [20]; [21].

In our recent studies, it has been demonstrated that the efficiency of photocatalytic hydrogen evolution activity can be enhanced by using anatase containing Cu/THS photocatalyst [22]. Furthermore, it was shown that the Cu loading on the surface of the THS particles played a crucial role on the activity of this composite photocatalyst. Moreover, it was shown that graphene also enhances the activity of the ternary Cu/THS/Graphene photocatalyst; again, it was found that the graphene content on the ternary Cu/THS/Graphene has a great effect on the activity on the ternary photocatalyst for solar-driven hydrogen evolution from glycerol reforming [23]. In the present study, we investigate the solar-driven photocatalytic reforming of glycerol for hydrogen production over ternary Cu/THS/Graphene catalysts; with great interest on the effect of process parameters such as initial glycerol concentration, pH, and photocatalyst dosage.

2. Methodology

The preparation of the photocatalysts and the catalytic H$_2$ production activity testing procedures are mentioned elsewhere [22]. The three photocatalysts prepared were THS, composite 0.5wt.%Cu/THS, and ternary 0.5wt.%Cu/THS/Graphene$_{anat}$. Both the composite and ternary photocatalysts were optimized from our previous studies, while studying the effect of Cu and graphene on the solar photocatalytic production of hydrogen activity from glycerol reforming [22]; [23]. The photocatalysts were characterized for SEM, XRD, UV-vis/DRS, and Photoluminescence (PL). The XRD analysis showed that all three catalysts contained 100% anatase THS particles; and no obvious peak of Cu or graphene was detected (results are not shown in this paper). In the next section, we discuss the SEM, UV-vis, and PL characterization of the three photocatalysts; we also discuss the solar photocatalytic hydrogen production activities of the three photocatalysts; as well as the effects of reaction parameters.

3. Results and Discussion

3.1. Characterization

3.1.1. SEM analysis

Figure 1 shows the SEM images of the prepared THS particles; composite 0.5wt.%Cu/THS; Elemental mapping of Cu nanoparticles dispersed on the surface of the THS particles; and the ternary 0.5wt.%Cu/THS/Graphene$_{anat}$. It can be observed from the picture that the THS were indeed achieved by the broken particle, which exposes its hollow chamber (insert). The main advantage of these THS is that they absorb light efficiently and produce multiple light reflections within the hollow chamber; and generate more electron/hole pairs [22]; [24]. The elemental mapping shows that the Cu nanoparticles are highly dispersed on the surface of the THS particles. This high dispersion of Cu nanoparticles allows the light photons to efficiently reach the surface of THS particles and photoexcite them in order to generate electron/hole pairs efficiently. The ternary Cu/THS/Graphene was successfully prepared as it can be seen from the picture, Figure 1(c). The Cu/THS composite particles are well dispersed and anchored on the inner and outer walls of the graphene sheets. The strong interaction between the Cu/THS composite particles and graphene sheets it attributed to the disconnection of the GO’s oxygen functional groups during calcination treatment, therefore resulting in the chemical bond between the Cu/THS composites and graphene sheets [25].
Figure 1. SEM imaging of: (a) The THS particles; (b) Elemental mapping of Cu nanoparticles dispersed on the surface of the THS particles; and (c) ternary 0.5wt.%Cu/THS/Graphene 4wt.%.

3.1.2. UV-vis/DRS and Photoluminescence Analysis
The UV-vis/DRS was employed to study the optical properties of the prepared samples, Figure 2 (left). The DRS plots show that there was a red shift in the absorption band edge into the visible light region, which suggested that the band gap was narrowed. Furthermore, a decrease in bandgap was achieved with Cu nanoparticles loading and the graphene; which increased the absorption efficiency of the visible light [22]; [23]; [26]; [27]. The rate electron/hole pair recombination of the prepared samples was then studied using photoluminescence (PL) analysis.

The PL analyses of the prepared samples are depicted in Figure 2 (right). The PL plots showed that the rate of recombination of the THS particles decreased after they were impregnated with Cu nanoparticles; and was further decreased graphene was introduced to the Cu/THS composite framework as shown by the weakening of the peaks intensities. The suppression in recombination rate is attributed to the Cu nanoparticles, which trap and transport the photoinduced electrons to the graphene sheets, which act as electron storage for facilitation of proton reduction into hydrogen molecules; whilst leaving the holes on the THS surface vacant for glycerol oxidation [23]; [22]; [28]; [29].

Figure 2. UV-vis/DRS analysis (left) and the photoluminescence analysis (right) of the prepared photocatalysts.

3.2. Photocatalytic Hydrogen production activity testing of the prepared photocatalysts
3.2.1. Effect of Cu and graphene loading
Figure 3 shows the photocatalytic hydrogen production activity of THS, composite Cu/THS, and ternary Cu/THS/Graphene photocatalysts. It can be observed that the activity of the THS particles increased exponentially after being loaded with Cu nanoparticles, and even increased further after the graphene was incorporated to its framework. The increase in the photocatalytic activity is attributed to high dispersion of Cu nanoparticles, which allows the light photons to reach the surface of the THS; the decrease in the bandgap and the suppression of the electron/hole recombination rate by both Cu nanoparticles and graphene sheets. The photocatalytic hydrogen evolution achieved for THS, Cu/THS, and Cu/THS/Graphene was 694 μmol.g<sub>cat</sub>⁻¹, 25140 μmol.g<sub>cat</sub>⁻¹, and 146824 μmol.g<sub>cat</sub>⁻¹, respectively.
Figure 3. Photocatalytic hydrogen production activity of THS, composite Cu/THS, and ternary Cu/THS/Graphene photocatalysts.

3.2.2. Effect of initial glycerol concentration

Figure 4 shows the effect of glycerol concentration on the photocatalytic production of H\textsubscript{2} activity over 0.5\text{wt.\%Cu/THS/graphene} and ternary Cu/THS/Graphene catalyst. It was observed from Figure 4(a) that the H\textsubscript{2} evolution increased with increasing glycerol concentration between 5 – 20 \text{\% (v/v)}, and levelled off when the glycerol concentration was increased to 25 \text{\% (v/v)}. The decrease in hydrogen evolution can be attributed to the presence of many glycerol molecules saturated on the active sites of the ternary photocatalyst; therefore, reducing the efficiency of electron/hole photogeneration, as well as the efficiency of glycerol oxidation [30]; [31]. Figure 4(b) depicts the initial hydrogen evolution rates (r\textsubscript{H2}) as a function of initial glycerol concentration; which were determined from the slopes of fitting lines in Figure 4(a). It was observed that the rates of hydrogen evolution with variation of glycerol concentrations obeys the Langmuir-Hinshelwood mechanism [31]; [32]; [33]. According to the reaction mode, r\textsubscript{H2} can be expressed as

\[
r_{\text{H2}} = k_{\text{H2}}K_{\text{Co}}/(1 + K_{\text{Co}})
\]

where \(k_{\text{H2}}\) is the rate constant of hydrogen evolution, \(K\) is the adsorption constant of glycerol, and \(C_{\text{o}}\) is the initial glycerol concentration. At low glycerol concentration (1 >> \(K_{\text{Co}}\), \(r_{\text{H2}}\) should be proportional to the glycerol concentration and therefore resulting in first-order with respect to glycerol with an apparent rate constant \(k_{\text{H2}}K\). At high concentration (1 << \(K_{\text{Co}}\), \(r_{\text{H2}}\) should remain constant resulting in zero-order kinetics. The inversion of equation (1) results in a linear plot, \(1/r_{\text{H2}} = 1/k_{\text{H2}} + 1/(k_{\text{H2}}K_{\text{Co}})\) as depicted in Figure 4(c); and it was observed that the calculated \(r_{\text{H2}}\) value fit well with the linear relationship and the \(k_{\text{H2}}\) and \(K\) were determined to be 0.051 mol.g\textsuperscript{-1}.h\textsuperscript{-1} and 0.162 L.mol\textsuperscript{-1}, respectively.
Figure 4. Effect of initial glycerol concentration on the photocatalytic hydrogen production activity of ternary 0.5wt.%Cu/THS/graphene4wt.% catalyst, (a) hydrogen evolution, (b) rates of hydrogen evolution, (c) linear plots of $\frac{1}{t_{H_2}}$ and the $k_{H_2}$.

3.2.3. Effect of pH

Solution pH is one of the most important parameter, which influences the photocatalytic hydrogen evolution, since it directly affects the surface charge of the photocatalyst and the sacrificial agent in the solution; resulting in a change of the electrostatic interaction between the photocatalyst surface and the sacrificial agent [34]; [35]. The influence of pH (2 - 10) on the photocatalytic hydrogen production from glycerol (10% v/v) reforming over a 0.5 wt.% Cu/THS/graphene4wt.% photocatalyst is shown in Figure 5. It was observed that the hydrogen production increased with increasing pH from 2 to 6, and decreased drastically with increasing pH above 6. These results suggested that the photocatalytic hydrogen production over the 0.5 wt.% Cu/THS/graphene4wt.% photocatalyst is most efficient under mild acidic conditions, with the best operating pH found to be 6.

The influence of the glycerol solution pH on the photocatalytic hydrogen evolution efficiency is complex. Therefore, it is important to understand the interaction between the glycerol molecules and active sites of the photocatalyst in order to put forward a plausible explanation. Since a ternary Cu/THS/graphene catalyst was employed in this study, an attempt to discuss the effect of pH on the individual components of the ternary catalyst will be made.

Firstly, it should be noted that the adsorption of glycerol onto the surface of the photocatalyst takes place through hydrogen bonding with the surface hydroxyl groups (TiOH) of the photocatalyst [36]; [37]. When the pH of the glycerol solution is extremely acidic (pH < 5), the surface charge of titania becomes positive; resulting in an electrostatic repulsion between the hydronium cations ($H^+$) present in the solution and the positively charged photocatalyst, which in turn reduces the adsorption efficiency of the hydronium cations; therefore, reducing the photocatalytic hydrogen evolution activity of the
photocatalyst. This is attributed to the ionization state of the surface of the catalyst according to the reaction equations below:

\[ \text{Ti}^{IV}\cdot\text{OH} + \text{H}^+ \rightarrow \text{Ti}^{IV}\cdot\text{OH}_2^+ , \quad \text{pH} < \text{pH}_{\text{PZC}} \quad (2) \]

\[ \text{Ti}^{IV}\cdot\text{OH} + \text{OH}^- \rightarrow \text{Ti}^{IV}\cdot\text{O}^- + \text{H}_2\text{O} \quad \text{pH} > \text{pH}_{\text{PZC}} \quad (3) \]

When the pH of the solution is high (pH > 7), the surface charge of titania is negative. Therefore, an electrostatic repulsion between a negatively charged titania and glycerol molecules occurs; retarding the glycerol adsorption on to the valence band holes for oxidation as well as the recombination of the photogenerated electron/hole pair. Furthermore, it is suggested that the photogenerated electron/hole pairs on the titania surface might recombine due to the negatively charged titania surface, which inhibits the migration of the photogenerated electrons [34]. It is widely reported that the point of zero charge (PZC) of titania occurs at pH of 5.8 – 6. [31]; [38]; [39]; [40]. Therefore, it is suggested that the efficient adsorption of glycerol molecules on to the active site of titania for enhanced oxidation can be achieved when the surface charge of titania is neutral; also the migration of photogenerated electrons to the conduction band is promoted, leading to an efficient photocatalytic activity (as shown on our results). It has been mentioned that the titania particles agglomerate under the acid conditions, resulting in less surface area exposed for glycerol adsorption and harvesting of photons; therefore, affecting the photocatalyst activity [41]. However, this agglomeration is not expected to occur with our ternary Cu/THS/graphene because the THS particles are well anchored on the surface of the graphene sheets. Furthermore, it is not expected that the THS particles will leach off the surface of the graphene. This is attributed to the surface charge of graphene, which is negative under both acidic and basic conditions; suggesting that the THS particles (which are positively charged under acidic conditions) will remain anchored on the surface of the graphene sheets [42]; [35]. Also, pH has a detrimental effect on the copper nanoparticles under extreme acidic conditions because under these conditions, the copper nanoparticles tend to leach off the surface of the titania into the solution [43]. Therefore, it can be concluded that at under extremely acidic conditions, the low photocatalyst activity is attributed to the electrostatic repulsion between THS nanoparticles and the glycerol molecules. While under the basic conditions, the low activity can be attributed to the light scattering of the THS particles because of the higher concentration of the OH− present in the system; as well as the poor migration of the photogenerated electrons to the conduction band due to the change in the surface charge of the THS particles [34]; [44].

**Figure 5.** Effect of pH on the photocatalytic hydrogen production activity of ternary 0.5wt.%Cu/THS/graphene4wt.% catalyst, (left) hydrogen evolution, (right) rates of hydrogen evolution.

3.2.4. Effect of catalyst dosage
The effect of catalyst dosage on the photocatalytic hydrogen activity of a ternary 0.5wt.%Cu/THS/graphene4wt.% catalyst was studied by varying the catalyst dosage between 20 – 120 mg. Figure 6 illustrate the effect of catalyst dosage on the photacatalytic activity of a ternary 0.5wt.%Cu/THS/graphene4wt.% photocatalyst for hydrogen evolution (left) as well as the rate of hydrogen evolution (right). It was observed that the hydrogen evolution increased with an increase in
catalyst dosage, with the maximum evolution (and rate of evolution) achieved with the catalyst dosage of 80 mg (50 ml of glycerol solution, 10% v/v); and a decrease in hydrogen evolution was observed with a catalyst dosage higher than 80 mg. The decrease in photocatalytic hydrogen evolution due to an increase in catalyst dosage can be attributed to aggregation of the photocatalyst particles, which reduces the active surface for efficient photons resulting in light scattering; and therefore, hindering the bulk of photons from reaching the active sites of the catalyst surface for efficient photogenerated electron/hole pair [45]; [46]; [47]; [48].

![Figure 6. Effect of catalyst dosage on the photocatalytic hydrogen production activity of ternary 0.5wt.%Cu/THS/graphene4wt.% catalyst, (a) hydrogen evolution, (b) rates of hydrogen evolution.](image)

**4. Conclusions**

In conclusion, it has been found that the photocatalytic hydrogen evolution activity of a ternary 0.5wt.%Cu/THS/graphene4wt.% photocatalyst is strongly influenced by initial glycerol concentration, pH, and photocatalyst dosage. An increase in initial glycerol concentration leads to a slightly linear increase in hydrogen production, and levels off when the concentration in increased above 10% (v/v); which is consistent with the Langmuir-Hinshelwood mechanism. The photocatalytic hydrogen evolution activity of the ternary catalyst is dependent on the influence of the pH on the surface charge of catalyst and the glycerol solution. The maximum rate of hydrogen evolution was achieved when the glycerol solution was slightly acidic (pH 6), which was attributed to charge of the THS particles (in the ternary catalyst, responsible for the photocatalytic generation of electron/hole pairs) which is almost neutral; therefore, able to adsorb and oxidize the glycerol molecules; and subsequently reduce the H+ into hydrogen molecules. Furthermore, the photogenerated electrons at the valence band can easily migrate to the conduction band, then to the surfaces of Cu nanoparticles and graphene sheets under slightly acidic conditions (pH 6). The photocatalytic hydrogen evolution activity increases with increasing photocatalyst dosage, and decreases when the photocatalyst is increased beyond the optimized catalyst dosage (80 mg/50ml of glycerol solution); because of the agglomeration of the catalyst particles, resulting in light scattering and the hindrance of efficient photons absorption for efficient photogeneration of electron/hole pairs.

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