Copper Nanowires as Highly Efficient and Recyclable Catalyst for Rapid Hydrogen Generation from Hydrolysis of Sodium Borohydride

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Abstract: Hydrogen (H2) is a clean energy carrier which can help to solve environmental issues with the depletion of fossil fuels. Sodium borohydride (NaBH4) is a promising candidate material for solid state hydrogen storage due to its huge hydrogen storage capacity and nontoxicity. However, the hydrolysis of NaBH4 usually requires expensive noble metal catalysts for a high H2 generation rate (HGR). Here, we synthesized high-aspect ratio copper nanowires (CuNWs) using a hydrothermal method and used them as the catalyst for the hydrolysis of NaBH4 to produce H2. The catalytic H2 generation demonstrated that 0.1 ng of CuNWs could achieve the highest volume of H2 gas in 240 min. The as-prepared CuNWs exhibited remarkable catalytic performance: the HGR of this study (2.7 × 10^10 mL min^-1 g^-1) is ~3.27 × 10^7 times higher than a previous study on a Cu-based catalyst. Furthermore, a low activation energy (Ea) of 42.48 kJ mol^-1 was calculated. Next, the retreated CuNWs showed an outstanding and stable performance for five consecutive cycles. Moreover, consistent catalytic activity was observed when the same CuNWs strip was used for four consecutive weeks. Based on the results obtained, we have shown that CuNWs can be a plausible candidate for the replacement of a costly catalyst for H2 generation.

Keywords: acetic acid; catalytic activity; energy efficiency; H2 spillover; metal nanowires; NaBH4

1. Introduction

Lately, many researchers have been exploring the use of metal nanocrystals in applications such as catalysis, electrocatalysis, sensor design, antimicrobial materials, and flexible transparent electrodes [1–7]. Nanocoppers (Cu) of one-dimensional shape have received attention due to their high electrical conductivity [8]. Compared with noble metals, Cu is much cheaper and abundant [9], making it an attractive option to replace the highly expensive and scarce noble metals in various applications [10]. Due to their large surface area-to-volume ratio, Cu nanocrystals are progressively studied for catalysis applications such as the reduction of nitrophenols and H2 generation from the hydrolysis of NaBH4 [11,12].

The excessive consumption of fossil fuels has led to the deterioration of the ecological environment and a severe energy crisis, which in turn has increased the intensity of the search for...
safe, efficient, and clean energy sources. \( \text{H}_2 \) is considered as a promising candidate to replace traditional fossil fuels due to its high energy density (142 MJ kg\(^{-1}\)) and renewability, and its environmentally friendly by-product (water)\[13,14\]. \( \text{H}_2 \) can be stored physically in liquid form or as a compressed gas. However, due to its low boiling and melting points, the pressure needed for the compression is too high which introduces the risk of leakage and explosion hazard\[15\]. Therefore, the lack of effectiveness, safety, and low cost of the \( \text{H}_2 \) carrier limits its commercial availability worldwide\[14\].

On the other hand, chemically storing \( \text{H}_2 \) in a solid state medium, such as a metal hydride, is potentially a safer and effective method\[15,16\]. There are several metal hydrides that have been utilized as chemical sources for \( \text{H}_2 \) production, including sodium borohydride (\( \text{NaBH}_4 \))\[17\] and lithium borohydride (\( \text{LiBH}_4 \))\[18\]. \( \text{NaBH}_4 \) is the most commonly utilized among all other metal hydrides because of its non-flammable and non-toxic nature\[15\]; it is also easy to be hydrolyzed\[19,20\], and its reaction product (\( \text{NaBO}_2 \)) is recyclable\[21\]. \( \text{NaBH}_4 \) also exhibits high gravimetric/volumetric \( \text{H}_2 \) storage capacity (10.8 wt%), which results in a high rate of \( \text{H}_2 \) production\[15,20,22\]. One mol of \( \text{NaBH}_4 \) can release 4 mol \( \text{H}_2 \) gas: \( \text{NaBH}_4 + 2 \text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4 \text{H}_2 \) (\( \Delta \text{H} = -217 \) kJ mol\(^{-1}\))\[21,23\].

However, the hydrolysis of \( \text{NaBH}_4 \) is slow at room temperature without a catalyst\[24\]. Therefore, various catalysts have been employed for the reaction\[14,24–27\]. Production of pure \( \text{H}_2 \) can be obtained by the hydrolysis of \( \text{NaBH}_4 \) with a controllable rate at ambient temperature with the presence of an appropriate catalyst. Previous studies showed that noble metals, such as platinum (\( \text{Pt} \))\[28\], ruthenium (\( \text{Ru} \))\[29\], and palladium (\( \text{Pd} \))\[30\], are effective catalysts for the hydrolysis of \( \text{NaBH}_4 \). Even though these catalysts show high stability and excellent catalytic activity, their expensive cost restrains their usage in wide applications\[31\]. The need to find durable, efficient, and cheap alternatives has led to further research works. Recently, there have been many studies done by using transition metal-based catalysts, such as cobalt\[32\], nickel\[33\], manganese\[26\], and \( \text{Cu} \)[12], to replace the noble metal catalysts. Some examples of transition metal-based catalysts are graphene-modified Co-B catalysts\[14\], Ni-Co-B hollow nanospheres\[34\], and cobalt boride@nickel/reduced graphene oxide (Co-B@Ni/RGO) nanocomposites\[35\]. Even though there are many studies related to \( \text{Cu} \) alloys or composites\[36–38\], there is only one study reported on the utilization of a \( \text{Cu} \)-based catalyst for the hydrolysis of \( \text{NaBH}_4 \)[12]. To the best of our knowledge, there has not been any study done as of this moment using CuNWs for the hydrolysis of \( \text{NaBH}_4 \) to generate \( \text{H}_2 \).

Even though there are advantages to using cheaper transition metals as catalysts, there are still several setbacks: these nanocatalysts are easy to aggregate which leads to a reduction in the specific surface area, thus causing a decrease in catalytic performance\[32\]. In addition, catalyst regeneration and leaching must also be addressed to increase the life span of the catalyst and availability for practical use. In this study, we synthesized copper nanowires (CuNWs) by a facile hydrothermal route, and we studied its catalytic performance in the hydrolysis of \( \text{NaBH}_4 \) to produce \( \text{H}_2 \) gas. Additionally, a short and simple treatment using glacial acetic acid (GAA) was conducted on the CuNWs. To avoid aggregation of the CuNWs during the catalytic reaction, the CuNWs were immobilized onto cotton cloth to improve the catalytic performance in terms of reusability, stability, and recoverability.

2. Materials and Methods

2.1. Materials

Copper chloride dihydrate (\( \text{CuCl}_2 \cdot 2\text{H}_2\text{O} \), \( \geq 99.0\% \)), octadecylamine (ODA, \( \text{C}_{18}\text{H}_{39}\text{N} \), \( \geq 85.0\% \)), sodium borohydride (\( \text{NaBH}_4 \), \( \geq 98\% \)), and chloroform (\( \text{CHCl}_3 \), \( \geq 99.8\% \)) were obtained from Merck. Ascorbic acid (AA, \( \text{C}_6\text{H}_8\text{O}_6 \), \( \geq 99\% \)) was obtained from Sigma. Glacial acetic acid (GAA, \( \text{CH}_3\text{COOH} \), 99.85%) was obtained from HmbG Chemicals. Sodium hydroxide (\( \text{NaOH} \), 99%) was obtained from SYSTERM. Cotton cloths (CC, 95% cotton) were cut into 0.5 × 1 cm\(^2\) for each hydrolysis reaction. All chemicals were used as received. All solutions were prepared with deionized water.
2.2. Synthesis of CuNWs

CuNWs were synthesized using a hydrothermal approach as reported previously [5]. Briefly, 26.3 mM of ODA, 2.8 mM of AA, and 5.6 mM of CuCl2·2H2O were dissolved in 30 mL of deionized water under stirring for 10 min and sonicated for 10 min. Next, the solution was transferred into a Teflon-lined autoclave and heated at 120 °C for 20 h. After the synthesis was done, the reddish-brown solution was washed with chloroform to separate CuNWs from other Cu products and kept in a sealed glass vial for further use.

2.3. Preparation of CuNWs Strips Samples

Different loadings of CuNWs (0.1 μg, 0.1 ng, 0.1 pg, and 0.1 fg) were drop-casted on cotton cloth strips (CuNWs/CC) and treated for 10 min using 10% GAA (GAA:isopropyl alcohol = 1:9) by dip coating. The CuNWs strips were kept in a sealed plastic bag and stored in a refrigerator.

2.4. Catalytic Study of H2 Generation

The kinetic studies of the hydrolysis of NaBH4 were carried out in a batch operation by the water displacement method, where the volume of H2 gas generated at a given interval is measured by reading the volume of the drained water in the cylindrical tube. In a typical measurement, 10 mL of 1 wt% NaBH4 that has been adjusted to pH 12 was prepared in a rubber sealed 50 mL conical flask. Then, a piece of CuNWs/CC with specific catalyst loading was put into the solution to initiate the catalytic reaction. The catalytic performance of the CuNWs/CC was tested by conducting several experiments at different pHs (10.45, 12, and 13), catalyst loadings (0.1 fg, 0.1 pg, 0.1 ng, and 0.1 μg), NaBH4 concentrations (0.1, 0.5, 1, 3, and 5 wt%), and reaction temperatures (298, 313, 323 and 333 K). Reusability and stability of the CuNWs/CC strips were investigated by repeating the GAA treatment using a freshly prepared NaBH4 solution. Continuous H2 generation by using a continuous flow system was also done by using 0.1 ng CuNWs with 10 mL of 1 wt% NaBH4. The continuous flow system was set up by using a syringe pump. NaBH4 was pumped at three different flow rates (2.5, 1.3, and 0.8 mL h−1) and passed through column reactor fitted on a HotCoil coil reactor (HotColumn™, Uniqsis, Cambridge, UK).

2.5. Characterization

The morphology of the CuNWs was analyzed by a field emission scanning electron microscope (FESEM, MERLIN ZEISS) and high-resolution transmission electron microscopy (HRTEM, FEI Technai G2 T20, Thermo Fisher, Waltham, MA, USA). The energy-dispersive X-ray (EDX) spectroscopy mapping was done by FESEM (FEI Quanta 400, Thermo Fisher). The chemical composition and crystal structure of the samples were examined by X-ray diffraction (XRD, Bruker D8 Advance) using Cu Kα radiation. The d-spacing (d) of the CuNWs was calculated using Bragg’s equation \( \lambda = 2d \sin \theta \), where \( \lambda \) is the wavelength of X-ray radiation used, \( \theta \) is the peak position angle, and \( d \) is the inter-planer distance.

3. Results

3.1. Characterization of CuNWs

The characterization of CuNWs using FESEM and XRD can be found from our previous study [5], where it can be seen that high-aspect ratio CuNWs (~2600) were successfully synthesized from the hydrothermal reaction. Figure S1a presents the HRTEM image of a nanowire that shows the lattice fringe spacing of 0.21 nm which corresponds to the d-spacing value of the (111) planes of fcc Cu [39,40] and is consistent with the previous XRD result. Figure S1b shows the EDX mapping of the Cu contents on the cotton cloth. It can be seen that there were only trace amounts of Cu added onto the cloth; due to the small size of the CuNWs, they could not be seen clearly among the fibers of the cotton cloth.
3.2. H₂ Production

3.2.1. Effects of pH

The hydrolysis of NaBH₄ can be significantly influenced by the pH and temperature of the reaction. Compared with pure water, the hydrolysis of NaBH₄ in water-alkaline solution is much slower due to the *in situ* simultaneous hydrolysis of sodium metaborate (NaBO₂) which leads to the formation of NaOH, as shown in Equations (1) and (2) [41,42]:

\[
\text{NaBH}_4(\text{aq}) + 2\text{H}_2\text{O}(l) \rightarrow \text{NaBO}_2(\text{aq}) + 4\text{H}_2(\text{g}) \quad (1)
\]

\[
\text{NaBO}_2(\text{aq}) + 2\text{H}_2\text{O}(l) \rightarrow \text{NaOH}(\text{aq}) + \text{H}_3\text{BO}_3(\text{aq}) \quad (2)
\]

The importance of pH makes it the first parameter tested in this study. Figure 1 shows the H₂ generation at three different pHs (10.45, 12, and 13). pH 10.45 was the initial value of the NaBH₄ solution without any adjustments. NaOH (0.1 M) was added to obtain pH 12 and pH 13. The H₂ generation at pH 10.45 and 12 was almost the same within the period of 240 min, meanwhile, at pH 13, the hydrolysis reaction was severely inhibited. This shows that H₂ generation can be greatly suppressed with the addition of alkali substances [43]. Table 1 shows the list of HGRs obtained from the hydrolysis of NaBH₄ at different pHs. It can be seen that the HGR value increased from pH 10.45 to 12, but decreased at pH 13. This is probably due to the involvement of OH⁻ in the hydrolysis of NaBH₄. The catalyzed hydrolysis of NaBH₄ can be accelerated with an appropriate increase in the NaOH concentration, thus enhancing the HGR. However, too much of NaOH could lead to a decrease in the solubility of NaBO₂, thus causing the subsequent precipitation from the solution, adherence on the surface of the catalyst, and blockage of the active sites [33,44]. This would then hinder the contact of BH₄⁻ with the catalyst surface, hence decreasing the hydrolysis rate [36]. With consideration of the real-life application in terms of the HGR, high H₂ capacity, and long shelf life of the fuel solution, pH 12 was chosen as the optimized pH of the NaBH₄ solution for further kinetics studies.

![Figure 1](image-url)  
*Figure 1.* Plot of H₂ generation versus time on the effect of different pH (conditions: 0.1 ng CuNWs, 10 mL of [NaBH₄] = 1 wt%, and temperature = 298 K).

| pH  | HGR (mL min⁻¹ g⁻¹ × 10⁻⁹) |
|-----|--------------------------|
| 10.45 | 2.38                     |
| 12   | 2.7                      |
| 13   | 0.1                      |

3.2.2. Effects of Catalyst Loading
In the present study, CuNWs were investigated as a catalyst for H2 generation from an alkaline NaBH4 solution. Therefore, the effect of the CuNWs' loadings was tested. Figure 2a shows the plot of H2 generation of different loadings of the catalyst with and without GAA treatment vs. time of reaction. It can be seen that there was very low H2 generation without GAA treatment on the CuNWs strips. This is probably due to the presence of residual ODA and a thin oxide layer on the surface of the CuNWs [9], which would prevent the direct contact of reactants with the active sites of the CuNWs. Even though the H2 generation using non-treated CuNWs strips was low, the total H2 generation in 240 min was slightly higher (19 mL) in comparison with when no catalyst was added to the solution (13 mL). After the treatment with GAA, the H2 generation increased significantly even with a very small amount of catalyst. This shows that the oxide and residual capping agent layers can be removed by using a short GAA treatment [45].

![Figure 2. Plot of (a) different copper nanowires' (CuNWs) loadings on H2 generation versus time; and (b) HGR versus CuNWs' loadings, both in logarithmic scale. (Conditions: 10 mL of [NaBH4] = 1 wt%, pH = 12, and temperature = 298 K).](image)

From Figure 2a, it can be seen that with the increase in catalyst loading (0–0.1 ng), the volume of H2 generation increases as well. When there was no catalyst added, the volume of H2 produced was only 13 mL in 240 min. According to the hydrolysis reactions, NaBH4 reacts slowly with water even without a catalyst to generate H2, even though it is not stable in air [43]. In comparison, when just a small amount of catalyst was added (0.1 fg), the volume of H2 generation increased significantly. In 240 min, the hydrolysis of NaBH4 for 0.1 fg, 0.1 pg, and 0.1 ng were 122, 158, and 176 mL, respectively. The enhancement in catalytic activity can be attributed to the increase in the specific surface area and more exposed active sites due to the addition of the CuNWs [17]. As the hydrolysis of NaBH4 proceeded, the rate in H2 generation started to decrease. During the hydrolysis process, the agglomeration of H2 and blockage of the active sites could impede the formation of new active sites for further catalytic cycles [17]. When the catalyst loading increased to 0.1 μg, only 134 mL of H2 gas was collected. This decrease in H2 generation is probably due to the agglomeration of excess CuNWs which could inhibit some of the active sites [46]. The rate of H2 generation was determined from the linear portion of each plot in Figure 2a. In this study, 0.1 ng was chosen as the fixed catalyst loading for the rest of the experiments due to easier handling and the volume of H2 generation obtained after 240 min was the highest. The HGR obtained for this study by using 0.1 ng CuNWs is $2.7 \times 10^9$, and this value is ~ $3.27 \times 10^7$ times higher than a previously reported Cu-based catalyst [12]. This indicates the importance of GAA treatment on CuNWs before the catalytic hydrolysis process. Figure 2b shows the values of the HGR versus the initial loadings of the CuNWs, both in logarithmic scale. The slope of the straight line is nearly zero (0.0465), indicating that the catalytic hydrolysis of NaBH4 is approximately zero order with respect to the catalyst loadings.
Presently, the dissociative chemisorption of BH$_4^-$ ions on the catalyst surface is generally accepted as the first kinetic step of the metal-catalyzed hydrolysis of NaBH$_4$ [34,47]. Holbrook and Twist [48] suggested that the H$_2$ was generated from both water and borohydride. Firstly, BH$_4^-$ ions are adsorbed on the electron-enriched Cu active sites of the CuNWs. The Cu-BH$_4^-$ ions then further dissociate to form Cu-BH$_3^-$ and Cu-H intermediates (Equation (3)). Subsequently, Cu-BH$_3^-$ reacts with H$_2$O, possibly via the BH$_3$ intermediate, to generate Cu-H and BH$_3$(OH)$^-$ (Equations (4)–(6)). After that, BH$_3$(OH)$^-$ undergoes a stepwise replacement of the B-H bonds by B-OH$^-$, which then finally yields B(OH)$_4^-$. Next, the Cu-H species combines with another Cu-H to afford H$_2$, and the active sites are regenerated (Equation (7)) [17,34].

$$2\text{Cu} + \text{BH}_4^- \leftrightarrow \text{Cu-BH}_3^- + \text{Cu-H} \quad (3)$$
$$\text{Cu-BH}_3^- \leftrightarrow \text{BH}_3 + \text{Cu} + \text{e}^-_{\text{Cu}} \quad (4)$$
$$\text{BH}_3 + \text{OH}^- \rightarrow \text{BH}_3(\text{OH})^- \quad (5)$$
$$\text{Cu} + \text{e}^-_{\text{Cu}} + \text{H}_2\text{O} \leftrightarrow \text{Cu-H} + \text{OH}^- \quad (6)$$
$$\text{Cu-H} + \text{Cu-H} \rightarrow 2\text{Cu} + \text{H}_2 \quad (7)$$

3.2.3. Effects of Concentrations of NaBH$_4$

The effect of the initial NaBH$_4$ concentration on the hydrolysis was studied by employing 0.1 ng CuNWs in an ambient condition. Figure 3a shows that the total H$_2$ generation was 35, 90, 176, 250, and 162 mL by using 0.1, 0.5, 1, 3, and 5 wt% NaBH$_4$, respectively. It can be seen that by increasing the NaBH$_4$ concentration from 0.1 to 3 wt%, the H$_2$ generation increased as well. However, at the NaBH$_4$ concentration of 5 wt%, the volume of H$_2$ generation decreased to 162 mL. This can also be seen with the HGR of the different concentrations of NaBH$_4$ (Table 2), where the HGR increases with the increase in the NaBH$_4$ concentrations (0.1–3 wt%), and then decreases when 5 wt% of NaBH$_4$ is used. For the rest of the experiments, the NaBH$_4$ concentration of 1 wt% was chosen for economic reasons.

![Figure 3. Plot of (a) different NaBH$_4$ concentrations (wt%) on H$_2$ generation versus time; and (b) HGR versus NaBH$_4$ concentrations, both in logarithmic scale. (Conditions: CuNWs = 0.1 ng, pH = 12, and temperature = 298 K).](image)
Table 2. List of HGR values of different NaBH₄ concentrations.

| Concentration of NaBH₄ (wt%) | HGR (mLmin⁻¹g⁻¹ × 10¹⁰) |
|-----------------------------|-------------------------|
| 0.1                         | 0.44                    |
| 0.5                         | 1.22                    |
| 1                           | 2.7                     |
| 3                           | 2.9                     |
| 5                           | 0.52                    |

Theoretically, a higher concentration of NaBH₄ is desired to achieve a high capacity of H₂. Therefore, when the NaBH₄ concentration used is less than the highest HGR obtained, more H₂O and BH₄⁻ can be in contact with the active sites on the surface of the catalyst to generate H₂ at higher NaBH₄ concentrations. However, NaBO₂ was produced simultaneously with H₂. Due to the low solubility of NaBO₂ under alkaline solution, NaBO₂ accumulation on the surface of the catalyst and solution would occur at higher initial NaBH₄ concentrations [46,49,50] Consequently, this will increase the solution viscosity [46,51] and further retard the mass transfer and decrease the H₂ generation [33]. At higher concentrations of NaBH₄, the insufficient active sites for the target reaction contributed to the lower catalytic performance [46].

Figure 3b shows the values of the HGR versus the initial concentration of NaBH₄ both in logarithmic scale. The HGR in the catalytic hydrolysis of NaBH₄ was calculated from the slope of each plot in the initial linear portion. Based on the slope of the straight line, it is indicating that the catalytic hydrolysis of NaBH₄ is 0.59 order with respect to the concentrations of NaBH₄, suggesting that the reaction follows fractional order kinetics with NaBH₄ [42]. Consequently, the rate law of each catalyst for the catalytic hydrolysis of NaBH₄ in this study can be given as in Equation (8):

\[-4d[NaBH₄]dt = d[H₂]dt = k[CuNWs]₀.⁰₅[NaBH₄]₀.⁵⁹ \] (8)

3.2.4. Effects of Temperature

Considering the fact that the reaction temperature is an important factor influencing the hydrolysis kinetics of NaBH₄, the effect of the reaction temperature was also investigated. Figure 4a shows the H₂ generation by using CuNWs as the catalyst at a temperature ranging from 298 to 333 K. It can be observed that the H₂ generation increases significantly with the reaction temperature. The time taken to reach a total volume of H₂ generation of 250 mL was 60, 30, and 9 min at 313, 323, and 333 K, respectively. At an elevated temperature, more active reacting molecules are available which caused the faster H₂ generation at a higher temperature [27].

![Graph showing the relationship between temperature and hydrogen generation](a)

![Graph showing the relationship between temperature and the natural logarithm of the reaction rate constant](b)

\[ y = -5109.3x + 15.44 \]

\[ R² = 0.77 \]

\[ E_a = 42.48 \text{ kJ/mol} \]
Figure 4. Plot of (a) different reaction temperatures on H₂ generation versus time; and (b) the Arrhenius plot, ln k versus 1/T. (Conditions: CuNWs = 0.1 ng, 10 mL of [NaBH₄] = 1 wt%, and pH = 12).

The rate constants of H₂ generation from the hydrolysis were measured from the linear portions of the H₂ generation plots of the four different temperatures. These values were then used for the calculation of the activation energy (E_a) from the Arrhenius plot. Figure 4b shows the plot of the log scale of rate constant and inverse temperature. The activation energy of NaBH₄ hydrolysis catalyzed by CuNWs was determined from the Arrhenius equation (Equation (9)):

\[ \ln k = \ln A - \frac{E_a}{RT} \]  

(9)

where k is the reaction rate, A is the Arrhenius constant, E_a is the activation energy (kJ mol⁻¹), R is the gas constant, and T is the absolute temperature (K). According to the slope of the straight line, the E_a obtained was 42.48 kJ mol⁻¹. This value is comparable to the other values reported by using other non-noble metal-based catalysts (Table 3). The lower E_a of this study shows that a fast hydrolysis reaction rate was successfully achieved [14]. This indicates that CuNWs are a good and efficient catalyst for the hydrolysis of NaBH₄.

| Catalyst | HGR (mL min⁻¹ g⁻¹) | E_a (kJ mol⁻¹) | Reference |
|----------|-------------------|---------------|-----------|
| Cobalt/iron(II,III) oxide@carbon (Co/FeOx@C) | 1403 | 49.2 | [46] |
| Nickel-cobalt-boride (Ni–Co–B) | 6400 | 33.1 | [34] |
| Reduced graphene oxide-nickel (rGO-Ni) | 33000 | - | [52] |
| Silver/multi walled carbon nanotubes (Ag/MWCNT) | 17.4 | 44.45 | [53] |
| Palladium/multi walled carbon nanotubes (Pd/MWCNT) | 23.0 | 62.66 | [30] |
| Copper-ferum-boride (Cu-Fe-B) | - | 57 | [36] |
| Molybdenum disulfide/palm oil waste activated carbon (MoS₂/POAC) | 1170.66 | 39.1 | [54] |
| Cobalt-ferum-cerium-chitosan-derived carbon (Co-Fe-C/Chi-C) | 4760 | 33.1 | [24] |
| Copper-molybdenum/three dimensional graphene oxide (Co-Mo/3DGO) | 7023.3 | 35.6 | [27] |
| Nickel-cobalt-phosphorus/γ-aluminium oxide (Ni-Co-P/γ-Al₂O₃) | 5180 | 52.05 | [50] |
| Cu based catalyst | 825 | 61.16 | [12] |
| Copper oxide/cobalt(II, III) oxide (CuO/CoOx) | 6162.55 | 56.38 | [37] |
| CuNWs (0.1 ng) | $2.7 \times 10^{10}$ | 42.48 | This study |

3.2.5. Reusability Test

The reusability of a catalyst is an important aspect to consider for stability, durability, and practical applications. Therefore, the reusability test of CuNWs as catalysts for the hydrolysis of NaBH₄ was studied under similar experimental conditions. Figure 5a,b shows the H₂ generation and HGR of the CuNWs without retreatment with GAA. By the second cycle, the catalytic performance of the CuNWs greatly decreased. In comparison with the first cycle where 176 mL of H₂ gas was collected in 240 min, the total volume of H₂ gas collected in the second cycle was only 16 mL. The volume of gas collected in the second cycle was only 9% of the initial cycle. This is probably due to the increase in boron products such as metaborate which hinder the accessibility of the active sites of the catalyst [36], thus decreasing its catalytic performance.
Figure 5. Plot of (a) H₂ generation versus time; and (b) HGR of the hydrolysis of NaBH₄ without retreatment of the CuNWs strips for two cycles, and (c) H₂ generation versus time; and (d) HGR of NaBH₄ with retreatment of the CuNWs using glacial acetic acid (GAA) in five consecutive cycles. (Conditions: CuNWs = 0.1 mg, 10 mL of [NaBH₄] = 1 wt%, pH = 12, and temperature = 298 K).

Due to the lower catalytic performance of the CuNWs in the second cycle of the NaBH₄ hydrolysis, the CuNWs strips were treated with GAA. Figure 5c,d shows the results of the reusability tests for the retreated CuNWs strips in five consecutive cycles. The volume of H₂ gas generation and the HGR were stable and consistent throughout the entire cycles without any noticeable differences. This efficient catalytic performance can be attributed to the good retention of the CuNWs on the cotton cloth which enabled the good recoverability of the CuNWs. Figure 6a,b shows the plot of the same CuNWs strip used as a catalyst for every week in a month. The total volume of H₂ generation and the HGR obtained in the span of a month were almost constant, which further shows the competence and stability of CuNWs as a catalyst in the hydrolysis of NaBH₄.
Figure 6. Plot of (a) H$_2$ generation versus time; and (b) HGR of the hydrolysis of NaBH$_4$ of the CuNWs strips for four weeks (conditions: CuNWs = 0.1 ng, 10 mL of [NaBH$_4$] = 1 wt%, pH = 12, and temperature = 298 K).

3.2.6. Catalytic Efficiency in Continuous Flow System

The key advantage of a continuous flow system is the ability to accurately control the reaction parameters for a scale-up laboratory reaction [55,56]. Hence, it is significant to measure the catalytic efficiency of the continuous flow system proposed. The experimental setup is illustrated in Figure 7. Table 4 shows the total production of H$_2$ obtained using the continuous flow system in the absence and presence of a catalyst at different flow rates. Based on Table 4, it can be seen that the H$_2$ production increased significantly with the presence of the CuNWs. When the flow rate decreased, the total volume of H$_2$ increased, which can be attributed to the increased retention time of the NaBH$_4$ solution in contact with the CuNWs [57]. At the same time, the yield of H$_2$ increased with the decrease in the flow rate applied. The results show that CuNWs can catalyze the hydrolysis of NaBH$_4$ by using a continuous flow system. Table 5 lists the HGR for different production methods, showing the excellent catalytic performance of CuNWs in the production of H$_2$ gas.

Figure 7. Schematic diagram of the continuous flow system setup for the production of H$_2$ (conditions: CuNWs = 0.1 ng, [NaBH$_4$] = 1 wt%, pH = 12, and temperature = 298 K).
Table 4. Total volume and yield of H\(_2\) produced with different flow rates (with and without CuNWs).

| Flow Rate (mL h\(^{-1}\)) | Volume of H\(_2\) in the Absence of CuNWs (mL) | Volume of H\(_2\) in the Presence of CuNWs (mL) | Yield of H\(_2\) in the Presence of CuNWs (%) |
|---------------------------|-----------------------------------------------|-----------------------------------------------|---------------------------------------------|
| 2.5                       | 9                                             | 49                                            | 18.85                                       |
| 1.3                       | 19                                            | 158                                           | 60.77                                       |
| 0.8                       | 26                                            | 238                                           | 91.54                                       |

Table 5. Comparison of HGR using different processes.

| Method                                      | HGR (mmol h\(^{-1}\)) | References |
|---------------------------------------------|------------------------|------------|
| Photo-fermentation                          | 0.16                   | [58]       |
| Direct bio-photolysis                       | 0.07                   | [59]       |
| Photocatalysis (visible light irradiation)  | 0.048                  | [60]       |
| Photocatalytic decomposition of ammonia borane | 0.022              | [61]       |
| Batch hydrolysis of NaBH\(_4\) \(^1\)       | 1.8                    |            |
| Continuous hydrolysis of NaBH\(_4\)(flow rate = 0.8 mL h\(^{-1}\)) | 0.6               | This work |

\(^1\) Conditions: CuNWs = 0.1 ng, [NaBH\(_4\)] = 1 wt%, pH = 12, and temperature = 298 K.

4. Conclusions

In this research work, a CuNWs catalyst was prepared by a simple hydrothermal method and used as a catalyst to produce H\(_2\) from the hydrolysis of NaBH\(_4\). An impressive catalytic performance was achieved by using a small amount (0.1 ng) of the catalyst, which yielded a high volume of H\(_2\) and the HGR was obtained. Furthermore, a low \(E_a\) (42.48 kJ mol\(^{-1}\)) was calculated which shows the excellent catalytic activity of CuNWs. The effectiveness of the GAA treatment on the CuNWs before each reusability cycle was also shown. Consequently, the stable and consistent H\(_2\) generation and HGR for the reusability test up to five cycles and stability test for four weeks suggests that CuNWs are a suitable catalyst for practical applications. The continuous production of H\(_2\) could be a potential supply for proton-exchange membrane fuel cells.

Supplementary Materials: The following are available online at www.mdpi.com/2079-4991/10/6/1153/s1. Figure S1: HRTEM and EDX mapping of the CuNWs/CC sample.

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