https://doi.org/10.1016/j.jallcom.2020.155429

Highly active and durable catalyst for hydrogen generation from $NaBH_4$ hydrolysis reaction: CoWB/NF nanodendrite with acicular array structure

Yongsheng Wei [a, b, *], Maosen Wang [a], Wenying Fu [a], Lu Wei [a], Xinsheng Zhao [a], Xiangyang Zhou [b], Meng Ni [c, *], Haijiang Wang [d, *]

[a] School of Physics and electronic engineering, Jiangsu Normal University, Xuzhou 221116, P.R. China

[b] Department of Mechanical and Aerospace Engineering, University of Miami, Coral Gables, FL 33124, USA

[c] Department of Building and Real Estate, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, P.R. China

[d] Department of Mechanical and Energy Engineering, Southern University of Science and Technology, Shenzhen 518055, P.R. China

* Corresponding author. E-mail: weiys@jsnu.edu.cn (Y. Wei); meng.ni@polyu.edu.hk (M. Ni); wanghj@sustech.edu.cn (H. Wang)

Abstract

Sodium borohydride ($NaBH_4$) hydrolysis is a promising technology to produce high purity hydrogen (H_2) on-site for fuel cells. However, the wide applications of this technology are hampered by the low catalytic activity and poor stability of catalyst for hydrogen production. To develop low-cost catalyst with high activity and good stability, a novel CoWB catalyst supported by nickel foam was prepared by pulse electrodeposition method for H_2 production from $NaBH_4$ alkaline solution. The SEM results revealed that the special microstructure of nanodendrite with acicular array, CoWB is uniformly plated on the surface of Ni foam (NF) substrate and firmly adhered to the surface. The tungsten doping decreased the activation energy to as low as 18.15 $kJ \cdot mol^{-1}$. The CoWB/NF catalyst exhibited higher hydrogen producing performance and the hydrogen generation rate (HGR) reached 14.13 $L \cdot min^{-1} \cdot g^{-1}$ cat, which was comparable to that of noble metal catalyst in literatures. More importantly, the catalyst demonstrated very good stability as the catalytic activity was maintained at 82% of its initial activity after 800 hours of usage. The CoWB/NF catalyst in hydrogen generator produced hydrogen with 99.9871% of purity at a HGR of 1.07 L/min. This study demonstrated that the novel CoWB/NF catalyst is very promising for hydrogen production from $NaBH_4$ hydrolysis reaction.

Keywords: Sodium borohydride, Hydrogen generation rate, CoWB/NF Nanodendrite, Acicular array, Pulse electrodeposition

1 Introduction

Hydrogen is a well-known energy carrier due to its abundance, high energy density and nature of being environment friendly[1]. Hydrogen can be used in light-weight proton exchange membrane fuel cell (PEMFC) for power generation at a high energy efficiency with the byproduct of water and heat. Therefore, PEMFC fueled with pure hydrogen has been considered as one of the most promising power sources for portable applications such as hydrogen fuel cell vehicles and unmanned aerial vehicles (UAV). However, lack of efficient and low-cost hydrogen production and storage is still a big challenge to the commercialization of fuel cell power systems. Sodium borohydride ($NaBH_4$) as a typical example of chemical hydrides has been considered as a safe and convenient hydrogen source due to its high hydrogen storage capacity (10.8 wt %), non-toxicity, ambient operation temperature, and controllability of the hydrolysis reaction [2-4].

However, the wide application of the $NaBH_4$ is impeded by the high cost (the use of noble metal catalyst) and relatively poor stability of the catalyst. Development of low-cost, durable and active catalyst for $NaBH_4$ hydrolysis reaction is thus the key to the efficient on-site hydrogen production for fuel cell applications. Hydrolysis of $NaBH_4$ is activated by various catalysts including platinum, rhodium, ruthenium[5], cobalt, and nickel. Platinum [6-8], rhodium, and ruthenium [7-16] are effective catalysts, but these catalysts are very expensive. Cobalt-based [17-39] and nickel-based [29-31, 40-42] show good catalytic activities and hydrogen production rates for the hydrolysis of $NaBH_4$. Co-B alloy and Co-B based catalysts are also considered to be good candidates for $NaBH_4$ hydrolysis owing to its satisfactory activity and low cost [24, 43-46]. However, the non-noble metal catalysts are usually less efficient than the noble metal catalyst and they may also suffer from poor stability for hydrogen production. Recently it has been found that CoWB catalyst is highly effective for catalyzing hydrogen generation from $NaBH_4$ alkaline solution [24, 47, 48]. However, CoWB also suffers from agglomeration phenomenon that limits its durability. It is expected that the catalyst activity and durability can be both enhanced by loading the catalyst on high-surface area supporting mateials or by doping suitable elements into the catalyst. Most of catalyst supports are porous

materials including NF(Nickel-form), carbon sphere, γ-Al_2O_3, honeycomb ceramics, etc. Among them, NF having porous structure, low areal density, and high thermal and chemical stability under the hydrolysis conditions is considered as one of the best supports for catalysts. In this work, novel CoWB catalyst supported by nickel foam was fabricated by a pulse electrodeposition (PED) method. The CoWB/NF catalyst synthesized using the method exhibited a high activity and durability towards hydrolysis reaction in $NaBH_4$ solution.

2 Experimental

2.1 Chemicals

NF was purchased from Hunan Liyuan New Martials Company. Cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, AR), sodium tungsten (Na_2WO_3, AR), sodium borohydride ($NaBH_4$, AR), sodium hydroxide (NaOH, AR) and ethylene glycol (EG, AR) were obtained from Sinopharm Chemical Reagent Co., Ltd. Alcohol and hydrochloric acid were purchased from Beijing Chemicals Ltd. Deionized water was used as the solvent whenever water is used in the synthesis and experiments.

2.2 Preparation

Nanodendatic stucture CoWB/NF catalysts were prepared by pulse electrodepostion (PED). The methods were similar to those given in our previous publications [49-51], as shown in Figure 1. Essentially, NF (Ni foam, 1 cm×1 cm) was firstly immersed in ethanol and ultrasonicated at 25 ℃ for 30 mins, removing the greasy dirt on the surface, followed by soaking in 10 vol.% HCl solution for 15 mins at room temperature to remove inorganic impurities. Finally, all the samples were cleaned by deionized water.

In a typical run, the pretreated NF was impregnated in the $CoCl_2$ EG solution for 3 hours, and then was plated in mixed 50 ℃ solution included Na_2WO_3, $NaBH_4$,and NaOH. Pulse electrodepostion current density is 200 mA/cm^2 at T_{on} time for 2ms, T_{off} time is 5ms, total plate time is 900s. The catalysts were thoroughly washed with ethanol and deionized water and were finally dried in vacuum oven at 323 K for 12 h. The prepared cayalyst was denoted as CoWB/NF.

2.3 Characterization

The composition of the CoWB/NF catalyst was performed by conventional X-ray powder diffraction (XRD) on a Rigaku D/MAX-RB diffractometer (Rigaku, Japan). Surface morphology of catalyst was studied by scanning electron microscopy (SEM, HITACHI S-4300, Japan) equipped with energy-dispersive spectroscopy analysis (EDS).

2.4 Hydrogen generation rate (HGR) test

The HGR was measured by a classical water-displacement method. Typically, the HGR was tested in a 100 mL three-neck flask immersed in a constant temperature bath. 10 mL aqueous solution consisting of $NaBH_4$ (5 wt.%) and NaOH (2 wt.%) was added into the flask at first, then CoWB/NF catalyst was put in rapidly to initiate the hydrolysis reaction under stirring. Volume of the evolved hydrogen was recorded by the volume of drained water of bird shaped bottle. Each measurement was repeated 3 times. The average HGR was normalized as $mL \cdot min^{-1} \cdot g^{-1}$ (CoWB).

$$HGR = \frac{V}{t*(m_2 - m_1)} \quad (1)$$

Where, m_1 is the weight of dried catalyst before PED, m_2 is the weight of dried catalyst after PED, t is the time of hydrogen producing, and V is the generated volume of hydrogen.

3 Results and Discussion

3.1 Catalyst characterization

The surface morphologies NF and CoWB/NF catalyst are shown in Figure 2(a). Compared to smooth surface of the NF, large area forest like catalyst coating observed on NF with nano-dendritic structure formed in pulse electrodeposition process. The enlarged photos clearly show us the CoWB grew up with nanosized dendritic structure in Figure 2 (c). TEM image shown in figure 2(e) further exhibits its nano-dendritic structure. The main reason is the CoWB/NF catalyst highly preferred orientation in the growth process by PED. This special structure could not only provide a favorable site for CoWB catalyst firmly rooted into NF, but also grow abundant of side branches which slit from the site providing more accessible active sites for the reactants [52]. AFM images shown in figure 2(j) display the nanostructure of acicular array in extremity of side branch. There are 167 peaks in 25 nm^2 area.

The average distance between peak to peak is 0.31 nm. This further proves that the dendritic structure has abundant branch tips as catalytic active sites.

Figure 2 (b) shows the sample energy dispersive spectra corresponding to selected zone in the CoWB catalyst indicated in the inset. The EDS analysis shows that the catalyst coating consisted of the three elements studied, namely Co, B and W, and their atomic ration is 51:19:3. Besides, the signal of the element C in the spectra can be attributed to the conductive adhesive introduced during the sample preparation. And that of the element O might come from the adsorbed oxygen or H_2O [47].

Figure 2 (d) shows X-ray diffraction (XRD) patterns of CoWB/NF catalyst. It is found that catalyst sample CoWB/NF was typical of crystalline phase structure with Ni sharp crystalline peaks at 2 theta values of 45^o, 52^o and 76^o. After pulse deposition, the as-synthesized CoWB/NF is an evolution of crystalline phase to an amorphous structure in the PED process.

As shown in figure 2(f-i), the surface species and electronic structures of CoWB/NF catalyst were studied by the X-ray photoelectron spectroscopy (XPS) measurement. The XPS results show clearly the peaks belonging to Co, W, B and Ni in the CoWB/NF NDs. The atomic ratio of Co, B, W is 51:17:1, which similar with the result of EDS measurement. In the deconvoluted XPS spectrum of Co 2p (figure 2(f)), two peaks located at 780.73 and 796.68 eV, are assigned to the binding energies of Co 2p3 and Co 2p1, which indicates the presence of metallic Co close to the electrode surface. Additionally, the peak centred at 780.9 ev is attributed to the main peak of oxidized Co 2p3. Figure 2(g) shows the W 4f spectrum, with the binding energies located at 34.73 eV is assigned to W 4f5, which exhibits a clear shift to lower value (33.5 eV for standard W 4f5). As well known, the d-band character of W dominates the band stucture of the catalyst surface and then affects the electrocayalytic activity to NaBH4 hydrolysis reaction. Figure 2(h) shows the B 1s spectrum, with the binding energies located at 191.68 eV is assigned to WB or Ni3B. The modification of the electronic structure appears after PED process, resulting d-band center upshift for the CoWB/NF NDs may alter the chemisorption of reactants, intermediates, and products and thus enhance the electrochemical performance in the hydrogen generation reaction.

3.2 Catalytic performance

3.2.1 Effect of mole fraction of W/Co in initial plating solution

The effect of mole fraction of W/Co in initial plating solution were studied as shown in Figure 3 (a-c). The as-prepared W doped alloy catalyst presents a high activity towards hydrolysis of $NaBH_4$ solution, but the catalytic activity is closely related to the W content in initial plating solution. It is because the XPS spectrum of W 4f5 happened shift when W was doped into the CoWB/NF catalyst in PED process, which leads to different catalytic effect. As shown in Figure 3(a), The CoWB/NF catalyst with mole fraction of W/Co of 40% shows the maximum catalytic activity. By using the optimized CoWB/NF catalyst, the 5wt.% $NaBH_4$+2wt.%NaOH solution can yield H_2 at an HGR of 1.711 $L \cdot min^{-1} \cdot g^{-1}$ at 30°C. The HGR of CoWB/NF catalyst increased with reaction temperature tightly, and the HGR reach as high as 14.13 $L \cdot min^{-1} \cdot g^{-1}$ (CoWB) at 70°C。Thanks to the doped W, the d-band character of W dominates the band stucture of the catalyst surface and then affects the electrocayalytic activity to $NaBH_4$ hydrolysis reaction. The activation energy results shown in figure 3 (c) also proved CoWB/NF has the lower value of 18.15 $kJ \cdot mol^{-1}$, leading the reaction easier to occur in $NaBH_4$ hydrolysis.

3.2.2 Solution uptake

It is necessary to consider the solution uptake in the porous catalyst for the hydrolysis of sodium borohydride. The porous structure provide reaction pathway and space for gas-liquid two phase flow of hydrogen gas and $NaBH_4$. At the same time the porous catalyst can maintain partially a mixed reaction solutions. It will take time to stop hydrogen gas produce on the surface of catalyst when the catalyst was taken out of the solution. The trailing time affect the control in hydrogen producing system. Figure 3 (d) shows the results of solution uptake in CoWB/NF catalyst. It could be found that solution uptake increased linearly with increasing the concentration from 5 wt. % to 25 wt.%. The main reason is that the porous catalyst holds almost the same volume solution and the higher concentration solution has bigger solution density. These results and conclusions are benefit for the design of H_2 generator.

3.2.3 Effect of $NaBH_4$ concentration

The rate of hydrogen generated versus the concentration of $NaBH_4$ in wt.% is given in Figure 3 (e). Effect of $NaBH_4$ concentration on the hydrogen generation rate was measured using x wt. % $NaBH_4$(x=5, 10, 15, 20, 25, 30, 35), 2 wt.% NaOH solution at 30^oC using CoWB/NF catalyst. As the $NaBH_4$ concentration increases from 5 wt. % to 35 wt.%, the average hydrogen generation rate decreases. The result is same as explained in literature [44]. The main reason is maybe that the porous structure is reasonable for $NaBH_4$ solution diffused to the surface of CoWB/NF catalyst with higher solution viscosity at higher $NaBH_4$ concentration, which is discourage for hydrogen generation on the interface between catalyst and solution.

3.2.4 Effect of NaOH concentration

The concentration of NaOH affects the hydrogen production from hydrolysis of $NaBH_4$ because the restrain effect. Figure 3(f) illustrates the hydrogen generation rate with different NaOH concentration, i.e. 0, 1, 2, 4, 8 wt. % in 10g of $NaBH_4$ solution with 30 wt.% $NaBH_4$ at 30^oC. When the NaOH concentration increased from 0 wt. % to 2 wt.%, the HGR decreased rapidly. This phenomenon is well known and can be explained [43]. The explanation of this phenomenon is the inhibition and stabilization effects of the hydroxyl ions in the $NaBH_4$ solution. Then, When the NaOH concentration changed from 2 wt.% to 8 wt.%, the HGR increased and then steady. The reason is that OH^- is involved in the hydrolysis of $NaBH_4$ and increase of NaOH concentration lead to decrease of $NaBO_2$ solubility and the subsequent precipitation from the solution and adherence on the catalyst surface. As a result, the hydrolysis reaction is hindered. In addition, the hydroxyl ions strongly complex water, thus decreasing the available free water needed for $NaBH_4$ hydrolysis [45].

3.2.5 Effect of solution temperature and activation energy

Influence of temperature on hydrogen generation rate in solutions containing 30 wt.% $NaBH_4$ and 2wt.% NaOH was investigated at temperatures ranging from 30^oC to 70^oC shown figure 3 (g, h). As expected, hydrogen generation rate increases with the temperature. Lowering NaOH concentration

had the inhibition effect in room temperature, this effect further enlarged at higher solution temperature.

The activation energy of hydrolysis of $NaBH_4$ in the presence of CoWB/NF catalyst in the temperature ranging from 30°C to 70°C is shown in Figure 3 (c), the value is as low as 18.15 kJ/mol in contrasting to 28 kJ/mol of Pd/C catalysts. Figure 4 shows that CoWB/NF catalyst had high HGR, which reached 14.13 $L \cdot min^{-1} \cdot g^{-1}$ cat at 70°C (30wt.% $NaBH_4$, 2wt.% NaOH), and was comparable to that noble metal catalysts in literatures [21, 46, 51, 53-57] shown in Table 1. With regards to the catalytic activity, the CoWB/NF catalyst seems to be superior to other non-noble metal catalysts, and even comparable to noble metal catalysts.

3.3 Durability

Catalyst durability is a crucial parameter for a practical hydrogen generation apparatus. In the present study, the CoWB/NF catalyst prepared by PED was tested for durability in continuous hydrogen production tests. After the catalytic hydrolysis reaction, the catalyst was separated from the byproduct solution, washed thoroughly with deionized water and reused. As seen in Figure 5 (a, b) the effect of $NaBH_4$ concentration was that the durability was better at higher $NaBH_4$ concentration with 300 hours test. After that, CoWB/NF catalyst showed better durability in continuous usage at the $NaBH_4$ concentration of 30 wt.% than that at lower concentrations. From figure 5(c, d), it could be found that even after 800 hours, the catalytic activity could retain 82% HGR of initial performance, 1.41 $L \cdot min^{-1} \cdot g^{-1}$ (cat). The main reason of decline was the production of the major by-product sodium metaborate that might lead to viscous solution to block the active catalytic sites and paths for hydrogen evolution form the surface of catalyst.

3.4 Hydrogen generation performance in generator

We designed and developed hydrogen generator based on the CoWB/NF catalyst and the physical photo is shown in figure 6 (a). The diameter and height size of this cylindrical system are both 20 cm. The hydrogen generation volume is linear increased and the rate is steady, the average rate is 1.07 L/min as shown in figure 6 (b). The hydrogen gas purity was tested by gas chromatography and the

results are shown in figue 6 (c, d). The FID front signal show us there are three impurity CH_4(0.0005%), C_2H_6(0.0006%), C_2H_4(0.0003%). TCD back signal tell that the main impurity is CO_2(0.0115%), and the hydrogen purity is H_2 (99.9871%). The souce of impurities maybe come from the $NaBH_4$ or NaOH raw material. The purity is high enough provided the hydrogen souce for fuel cell, and the hydrogen generation rate could be supply hydrogen for 100 w fuel cell system.

4 Conclusions

By using the pulse electrodeposition method, the CoWB catalyst supported on NF was prepared for catalyzing hydrogen generation from alkaline $NaBH_4$ solution. The developed catalyst showed high HGR. More interestingly, the durability of CoWB/NF catalyst was impressive too. Even after 800 hours of usage, 82% HGR of the initial HGR could be retained. The present work reveals that CoWB catalyst supported on NF could be used in practical $NaBH_4$–based hydrogen generator for portable fuel cell system with a high catalytic activity and high durability.

Acknowledgments

This work was financially supported National Natural Science Foundation of China (No.21606115), Shenzhen Peacock Plan (KQTD2016022620054656), Development and Reform Commission of Shenzhen Municipality (2017) No. 1106 and Guangdong Innovative and Entrepreneurial Research Team Program (2016ZT06N500). Prof. Meng Ni would thank the grant (Project Number: PolyU 152214/17E) from Research Grant Council, University Grants Committee, Hong Kong SAR.

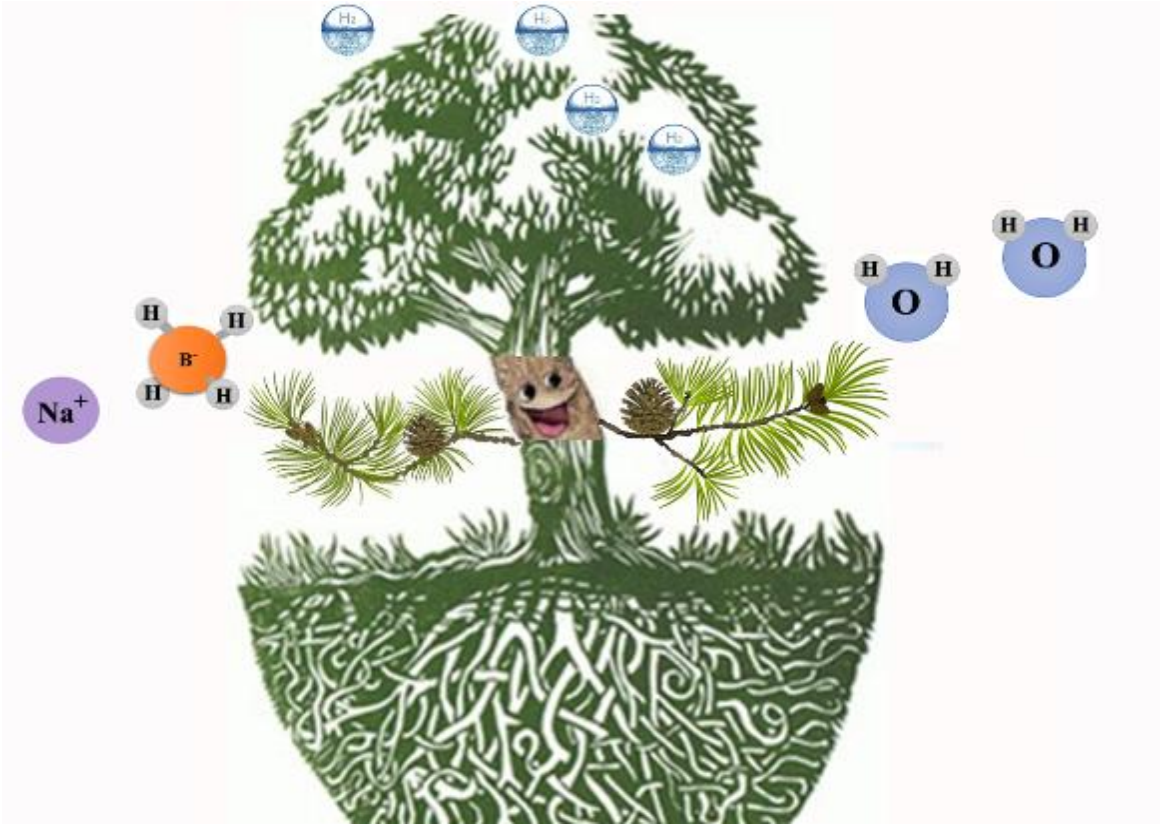
References

[1] Luo YT, Tang L, Khan U, Yu QM, Cheng HM, Zou XL, et al. Morphology and surface chemistry engineering toward pH-universal catalysts for hydrogen evolution at high current density. Nat Commun. 2019;10:1-9.
[2] Bhattacharjee D, Dasgupta S. Trimetallic NiFePd nanoalloy catalysed hydrogen generation from alkaline hydrous hydrazine and sodium borohydride at room temperature. J Mater Chem A. 2015;3:24371-8.
[3] Wang SH, Fan YA, Chen MQ, Xie YY, Wang DW, Su CY. Porous Co-P-Pd nanotube arrays for hydrogen generation by catalyzing the hydrolysis of alkaline NaBH4 solution. J Mater Chem A. 2015;3:8250-5.
[4] Liu TT, Wang KY, Du G, Asiri AM, Sun XP. Self-supported CoP nanosheet arrays: a non-precious metal catalyst for efficient hydrogen generation from alkaline NaBH4 solution. J Mater Chem A. 2016;4:13053-7.
[5] Tuan DD, Lin KYA. Ruthenium supported on ZIF-67 as an enhanced catalyst for hydrogen generation from hydrolysis of sodium borohydride. Chem Eng J. 2018;351:48-55.
[6] Kojima Y, Suzuki K, Fukumoto K, Sasaki M, Yamamoto T, Kawai Y, et al. Hydrogen generation using sodium borohydride solution and metal catalyst coated on metal oxide. Int J Hydrogen Energ. 2002;27:1029-34.
[7] Krishnan P, Yang TH, Lee WY, Kim CS. PtRu-LiCoO2 - an efficient catalyst for hydrogen generation from sodium borohydride solutions. J Power Sources. 2005;143:17-23.

[8] Liu ZL, Guo B, Chan SH, Tang EH, Hong L. Pt and Ru dispersed on LiCoO(2) for hydrogen generation from sodium borohydride solutions. J Power Sources. 2008;176:306-11.
[9] Amendola SC, Sharp-Goldman SL, Janjua MS, Spencer NC, Kelly MT, Petillo PJ, et al. A safe, portable, hydrogen gas generator using aqueous borohydride solution and Ru catalyst. Int J Hydrogen Energ. 2000;25:969-75.
[10] Amendola SC, Sharp-Goldman SL, Janjua MS, Kelly MT, Petillo PJ, Binder M. An ultrasafe hydrogen generator: aqueous, alkaline borohydride solutions and Ru catalyst. J Power Sources. 2000;85:186-9.
[11] Xia ZT, Chan SH. Feasibility study of hydrogen generation from sodium borohydride solution for micro fuel cell applications. J Power Sources. 2005;152:46-9.
[12] Zhang JS, Delgass WN, Fisher TS, Gore JP. Kinetics of Ru-catalyzed sodium borohydride hydrolysis. J Power Sources. 2007;164:772-81.
[13] Demirci UB, Garin F. Ru-based bimetallic alloys for hydrogen generation by hydrolysis of sodium tetrahydroborate. J Alloy Compd. 2008;463:107-11.
[14] Liang Y, Dai HB, Ma LP, Wang P, Cheng HM. Hydrogen generation from sodium borohydride solution using a ruthenium supported on graphite catalyst. Int J Hydrogen Energ. 2010;35:3023-8.
[15] Huang YH, Su CC, Wang SL, Lu MC. Development of Al2O3 carrier-Ru composite catalyst for hydrogen generation from alkaline NaBH4 hydrolysis. Energy. 2012;46:242-7.
[16] Huang ZM, Su A, Liu YC. Hydrogen generator system using Ru catalyst for PEMFC (proton exchange membrane fuel cell) applications. Energy. 2013;51:230-6.
[17] Jeong SU, Kim RK, Cho EA, Kim HJ, Nam SW, Oh IH, et al. A study on hydrogen generation from NaBH4 solution using the high-performance Co-B catalyst. J Power Sources. 2005;144:129-34.
[18] Wu C, Wu F, Bai Y, Yi BL, Zhang HM. Cobalt boride catalysts for hydrogen generation from alkaline NaBH4 solution. Mater Lett. 2005;59:1748-51.
[19] Patel N, Guella G, Kale A, Miotello A, Patton B, Zanchetta C, et al. Thin films of Co-B prepared by pulsed laser deposition as efficient catalysts in hydrogen producing reactions. Appl Catal a-Gen. 2007;323:18-24.
[20] Cho KW, Kwon HS. Effects of electrodeposited Co and Co-P catalysts on the hydrogen generation properties from hydrolysis of alkaline sodium borohydride solution. Catal Today. 2007;120:298-304.
[21] Lee J, Kong KY, Jung CR, Cho E, Yoon SP, Han J, et al. A structured Co-B catalyst for hydrogen extraction from NaBH4 solution. Catal Today. 2007;120:305-10.
[22] Mitov M, Rashkov R, Atanassov N, Zielonka A. Effects of nickel foam dimensions on catalytic activity of supported Co-Mn-B nanocomposites for hydrogen generation from stabilized borohydride solutions. J Mater Sci. 2007;42:3367-72.
[23] Kim SJ, Lee J, Kong KY, Jung CR, Min IG, Lee SY, et al. Hydrogen generation system using sodium borohydride for operation of a 400 W-scale polymer electrolyte fuel cell stack. J Power Sources. 2007;170:412-8.
[24] Dai HB, Liang Y, Wang P, Yao XD, Rufford T, Lu M, et al. High-performance cobalt-tungsten-boron catalyst supported on Ni foam for hydrogen generation from alkaline sodium borohydride solution. Int J Hydrogen Energ. 2008;33:4405-12.
[25] Krishnan P, Advani SG, Prasad AK. Cobalt oxides as Co2B catalyst precursors for the hydrolysis of sodium borohydride solutions to generate hydrogen for PEM fuel cells. Int J Hydrogen Energ. 2008;33:7095-102.
[26] Huang YQ, Wang Y, Zhao RX, Shen PK, Wei ZD. Accurately measuring the hydrogen generation rate for hydrolysis of sodium borohydride on multiwalled carbon nanotubes/Co-B catalysts. Int J Hydrogen Energ. 2008;33:7110-5.
[27] Patel N, Fernandes R, Guella G, Kale A, Miotello A, Patton B, et al. Structured and nanoparticle assembled Co-B thin films prepared by pulsed laser deposition: A very efficient catalyst for hydrogen production. J Phys Chem C. 2008;112:6968-76.
[28] Eom K, Cho K, Kwon H. Effects of electroless deposition conditions on microstructures of cobalt-phosphorous catalysts and their hydrogen generation properties in alkaline sodium borohydride solution. J Power Sources. 2008;180:484-90.
[29] Kim DR, Cho KW, Choi YI, Park CJ. Fabrication of porous Co-Ni-P catalysts by electrodeposition and their catalytic characteristics for the generation of hydrogen from an alkaline NaBH4 solution. Int J Hydrogen Energ. 2009;34:2622-30.
[30] Fernandes R, Patel N, Miotello A. Efficient catalytic properties of Co-Ni-P-B catalyst powders for hydrogen generation by hydrolysis of alkaline solution of NaBH4. Int J Hydrogen Energ. 2009;34:2893-900.
[31] Fernandes R, Patel N, Miotello A, Filippi M. Studies on catalytic behavior of Co-Ni-B in hydrogen production by hydrolysis of NaBH4. J Mol Catal a-Chem. 2009;298:1-6.
[32] Patel N, Fernandes R, Miotello A. Hydrogen generation by hydrolysis of NaBH4 with efficient Co-P-B catalyst: A kinetic study. J Power Sources. 2009;188:411-20.
[33] Chen Y, Kim H. Preparation and application of sodium borohydride composites for portable hydrogen production. Energy. 2010;35:960-3.
[34] Eom K, Kwon H. Effects of deposition time on the H-2 generation kinetics of electroless-deposited cobalt-phosphorous catalysts from NaBH4 hydrolysis, and its cyclic durability. Int J Hydrogen Energ. 2010;35:5220-6.
[35] Zhang XW, Zhao JZ, Cheng FY, Liang J, Tao ZL, Chen J. Electroless-deposited Co-P catalysts for hydrogen generation from alkaline NaBH4 solution. Int J Hydrogen Energ. 2010;35:8363-9.
[36] Simagina VI, Komova OV, Ozerova AM, Netskina OV, Odegova GV, Kellerman DG, et al. Cobalt oxide catalyst for hydrolysis of sodium borohydride and ammonia borane. Appl Catal a-Gen. 2011;394:86-92.

[37] Oh TH, Kwon S. Effect of manufacturing conditions on properties of electroless deposited Co-P/Ni foam catalyst for hydrolysis of sodium borohydride solution. Int J Hydrogen Energ. 2012;37:15925-37.
[38] Oh TH, Kwon S. Effect of bath composition on properties of electroless deposited Co-P/Ni foam catalyst for hydrolysis of sodium borohydride solution. Int J Hydrogen Energ. 2012;37:17027-39.
[39] Oh TH, Kwon S. Performance evaluation of hydrogen generation system with electroless-deposited Co-P/Ni foam catalyst for NaBh(4) hydrolysis. Int J Hydrogen Energ. 2013;38:6425-35.
[40] Kim JH, Kim KT, Kang YM, Kim HS, Song MS, Lee YJ, et al. Study on degradation of filamentary Ni catalyst on hydrolysis of sodium borohydride. J Alloy Compd. 2004;379:222-7.
[41] Pinto AMFR, Falcao DS, Silva RA, Rangel CM. Hydrogen generation and storage from hydrolysis of sodium borohydride in batch reactors. Int J Hydrogen Energ. 2006;31:1341-7.
[42] Zhang QL, Wu Y, Sun XL, Ortega J. Kinetics of catalytic hydrolysis of stabilized sodium borohydride solutions. Ind Eng Chem Res. 2007;46:1120-4.
[43] Tian HJ, Guo QJ, Xu DY. Hydrogen generation from catalytic hydrolysis of alkaline sodium borohydride solution using attapulgite clay-supported Co-B catalyst. J Power Sources. 2010;195:2136-42.
[44] Ozdemir E. Enhanced catalytic activity of Co-B/glassy carbon and Co-B/graphite catalysts for hydrolysis of sodium borohydride. Int J Hydrogen Energ. 2015;40:14045-51.
[45] Wang Y, Li TL, Bai SC, Qi KZ, Cao ZQ, Zhang K, et al. Catalytic hydrolysis of sodium borohydride via nanostructured cobalt-boron catalysts. Int J Hydrogen Energ. 2016;41:276-84.
[46] Cui ZK, Guo YP, Ma JT. In situ synthesis of graphene supported Co-Sn-B alloy as an efficient catalyst for hydrogen generation from sodium borohydride hydrolysis. Int J Hydrogen Energ. 2016;41:1592-9.
[47] Dai HB, Liang Y, Wang P. Effect of trapped hydrogen on the induction period of cobalt-tungsten-boron/nickel foam catalyst in catalytic hydrolysis reaction of sodium borohydride. Catal Today. 2011;170:27-32.
[48] Ekinci A, Sahin O, Saka C, Avci T. The effects of plasma treatment on electrochemical activity of Co-W-B catalyst for hydrogen production by hydrolysis of NaBH4. Int J Hydrogen Energ. 2013;38:15295-301.
[49] Wei YS, Wang R, Meng LY, Wang Y, Li GD, Xin SG, et al. Hydrogen generation from alkaline NaBH4 solution using a dandelion-like Co-Mo-B catalyst supported on carbon cloth. Int J Hydrogen Energ. 2017;42:9945-51.
[50] Wei YS, Huang XK, Wang JY, Yu HY, Zhao XS, Cheng DJ. Synthesis of bifunctional non-noble monolithic catalyst Co-W-P/carbon cloth for sodium borohydride hydrolysis and reduction of 4-nitrophenol. Int J Hydrogen Energ. 2017;42:25860-8.
[51] Wei YS, Wang Y, Wei L, Zhao XS, Zhou XY, Liu HT. Highly efficient and reactivated electrocatalyst of ruthenium electrodeposited on nickel foam for hydrogen evolution from NaBH4 alkaline solution. Int J Hydrogen Energ. 2018;43:592-600.
[52] Wang JL, Chen FY, Jin YC, Lei YM, Johnston RL. One-Pot Synthesis of Dealloyed AuNi Nanodendrite as a Bifunctional Electrocatalyst for Oxygen Reduction and Borohydride Oxidation Reaction. Adv Funct Mater. 2017;27.
[53] Bai Y, Wu CA, Wu F, Yi BL. Carbon-supported platinum catalysts for on-site hydrogen generation from NaBH4 solution. Mater Lett. 2006;60:2236-9.
[54] Patel N, Patton B, Zanchetta C, Fernandes R, Guella G, Kale A, et al. Pd-C powder and thin film catalysts for hydrogen production by hydrolysis of sodium borohydride. Int J Hydrogen Energ. 2008;33:287-92.
[55] Baydaroglu F, Ozdemir E, Hasimoglu A. An effective synthesis route for improving the catalytic activity of carbon-supported Co-B catalyst for hydrogen generation through hydrolysis of NaBH4. Int J Hydrogen Energ. 2014;39:1516-22.
[56] Guo YP, Dong ZP, Cui ZK, Zhang XJ, Ma JT. Promoting effect of W doped in electrodeposited Co-P catalysts for hydrogen generation from alkaline NaBH4 solution. Int J Hydrogen Energ. 2012;37:1577-83.
[57] Wang LN, Li Z, Zhang PP, Wang GX, Xie GW. Hydrogen generation from alkaline NaBH4 solution using Co-Ni-Mo-P/gamma-Al2O3 catalysts. Int J Hydrogen Energ. 2016;41:1468-76.

Graphical abstract



Highlights

- CoWB/NF nanodendrite catalyst with acicular array structure was prepared by pulse electrodeposition method.
- CoWB/NF catalyst has lower activation energy (18.15 $kJ \cdot mol^{-1}$) and higher HGR (14.13 $L \cdot min^{-1} \cdot g^{-1}$) for $NaBH_4$ Hydrolysis Reaction.
- The catalyst exhibited 800 hours long-term stability and 99.9871% of purity at a HGR of 1.07 L/min.

Table

Table 1 A comparison on the HGR and E_a between the CoWB/NF catalyst and the published results of other noble metal or non-noble metal catalysts

Catalyst	Reaction condition			HGR	E_a	Ref
	T (℃)	$NaBH_4$ (wt.%)	NaOH (wt.%)	($L \cdot min^{-1} \cdot g^{-1}$ cat.)	($kJ \cdot mol^{-1}$)	
Pt/C	40	10	5	23	-	[53]
Pd/C	25	1	5	23	28	[54]
Ru/NF	30	5	2	23.03	39.48	[51]
Co-B/C	30	10	5	10.82	56.7	[55]
Co–W–P/Cu	30	10	10	5	22.8	[56]
Co–B/NF	20	25	3	7.2	-	[21]
Co-Ni-Mo-P/γ-Al_2O_3 (0.5 $g \cdot L^{-1}$)	30	7	10	3.68	52.43	[57]
Co-Sn-B/GP	30	5	5	11.27	39.57	[46]
CoWB/NF	70	30	2	14.13	18.15	Our work

Figure Captions

Figure 1. Schematic illustration of CoWB/NF Nanodendrites catalyst by pulse electrodeposition

Figure 2 General characterization of CoWB/NF catalyst. **(a, c)** SEM morphologies of CoWB/NF **(b)** EDS of CoWB/NF **(d)** XRD of CoWB/NF **(e)** TEM image of CoWB/NF **(f-i)** The XPS survey of CoWB/NF catalyst **(j)** AFM image of CoWB/NF

Figure 3 (a) Effect of mole fraction of W/Co in initial solution on HGR at different temperature **(b,c)** Activation Energy of CoWB/NF catalyst at different mole fraction of W/Co **(d)** Solution uptake in CoWB/NF catalyst **(e, f, g)** H_2 generation rate at different $NaBH_4$ concentration, NaOH content, reaction temperature. **(h)** Influence curve of NaOH content in solution at different reaction temperature (Typical Conditions: 10g of reaction solution include 30wt.% $NaBH_4$+2wt.%NaOH, 30^{o}C)

Figure 4 HGR and Activation energy of CoWB/NF catalyst comparation with literatures[21, 46, 51, 53-57]

Figure 5 Effect of $NaBH_4$ concentration on catalytic durability

Figure 6 (a) Hydrogen generator physical photo **(b)** Hydrogen generation rate and temperature of Hydrogen gas **(c, d)** Gas purity detection results with FID and TCD

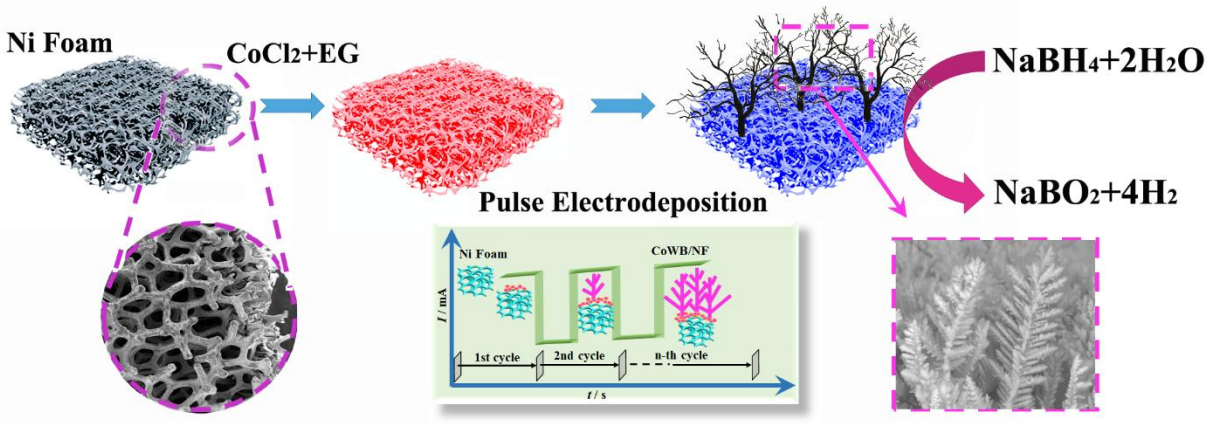

Ni Foam
CoCl2+EG
Pulse Electrodeposition
NaBH4+2H2O
NaBO2+4H2
Ni Foam
CoWB/NF
I / mA
1st cycle
2nd cycle
n-th cycle
t / s

Figure 1

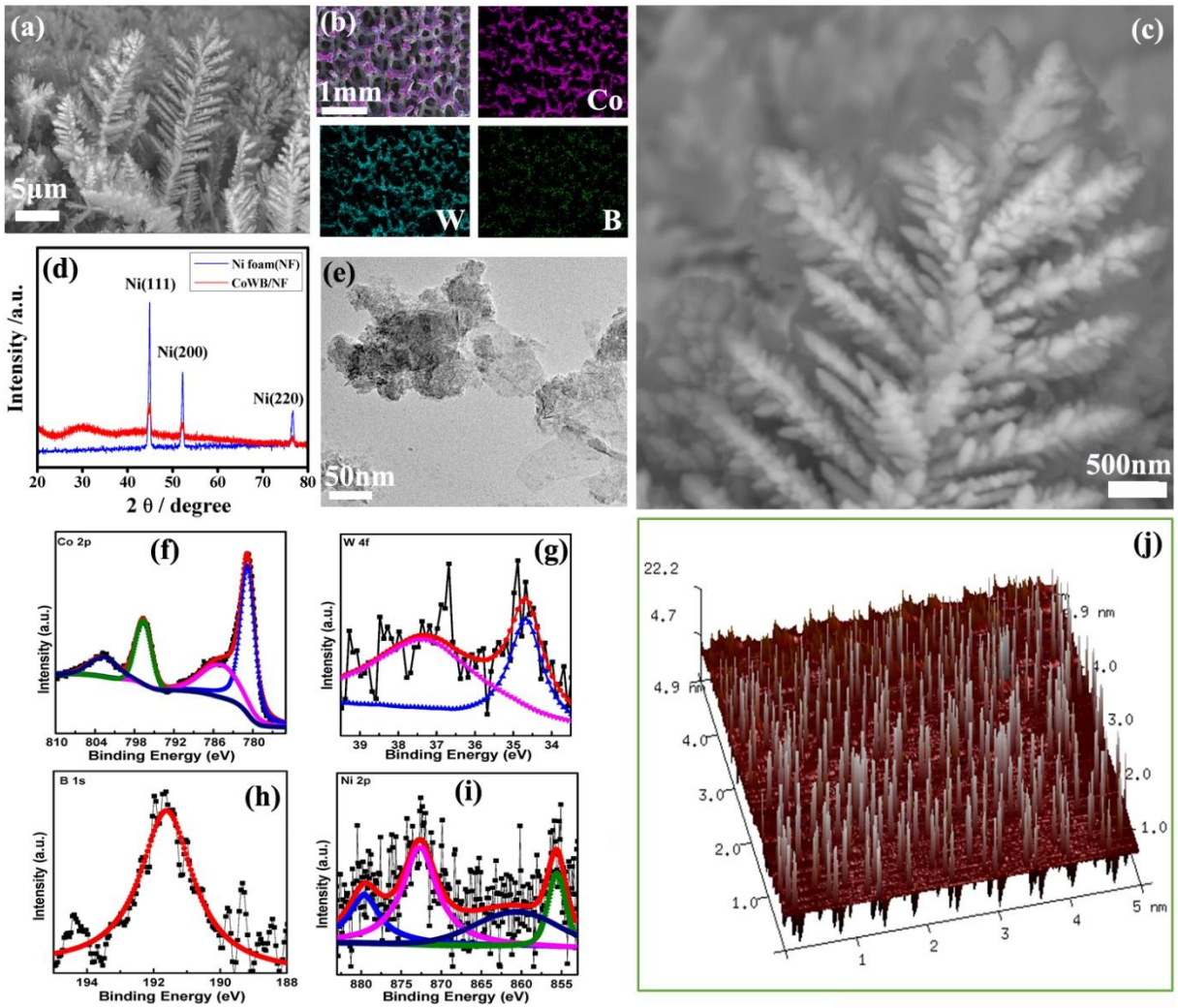

(a)
5μm
(b)
1mm
Co
W
B
(c)
500nm
(d)
Ni foam(NF)
CoWB/NF
Ni(111)
Ni(200)
Ni(220)
Intensity /a.u.
2 θ / degree
(e)
50nm
(f)
Co 2p
Intensity (a.u.)
Binding Energy (eV)
(g)
W 4f
Intensity (a.u.)
Binding Energy (eV)
(h)
B 1s
Intensity (a.u.)
Binding Energy (eV)
(i)
Ni 2p
Intensity (a.u.)
Binding Energy (eV)
(j)
22.2
4.7
4.9 nm
4.0
3.0
2.0
1.0
5 nm

Figure 2

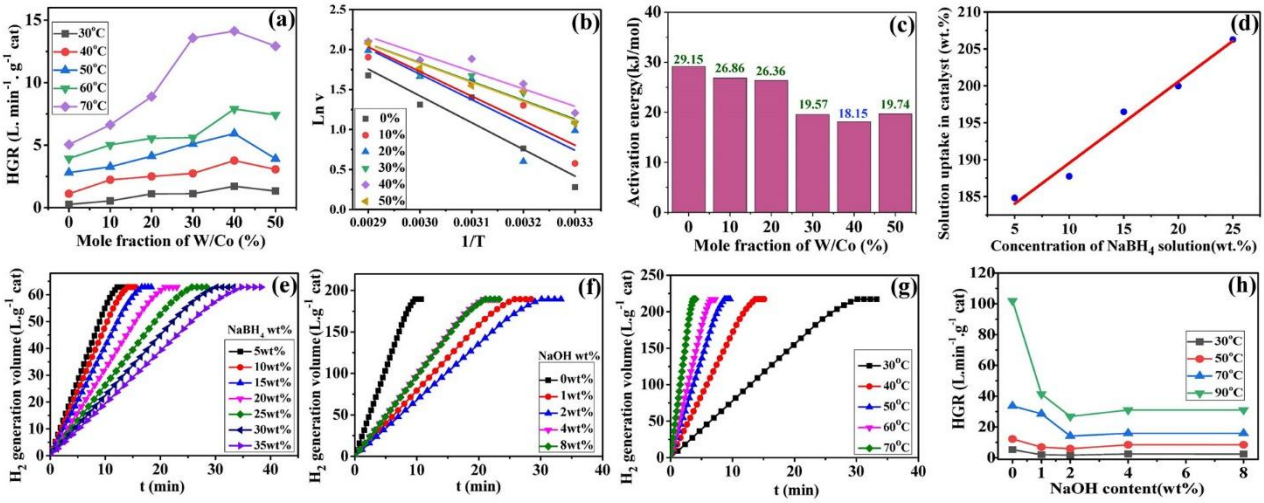

(a)
HGR (L. min^{-1} . g^{-1} cat)
30°C
40°C
50°C
60°C
70°C
Mole fraction of W/Co (%)
(b)
Ln v
0%
10%
20%
30%
40%
50%
1/T
(c)
Activation energy(kJ/mol)
29.15
26.86
26.36
19.57
18.15
19.74
Mole fraction of W/Co (%)
(d)
Solution uptake in catalyst (wt.%)
Concentration of NaBH$_4$ solution(wt.%)
(e)
H$_2$ generation volume(L.g^{-1} cat)
NaBH$_4$ wt%
5wt%
10wt%
15wt%
20wt%
25wt%
30wt%
35wt%
t (min)
(f)
H$_2$ generation volume(L.g^{-1} cat)
NaOH wt%
0wt%
1wt%
2wt%
4wt%
8wt%
t (min)
(g)
H$_2$ generation volume(L.g^{-1} cat)
30°C
40°C
50°C
60°C
70°C
t (min)
(h)
HGR (L.min^{-1}.g^{-1} cat)
30°C
50°C
70°C
90°C
NaOH content(wt%)

Figure 3

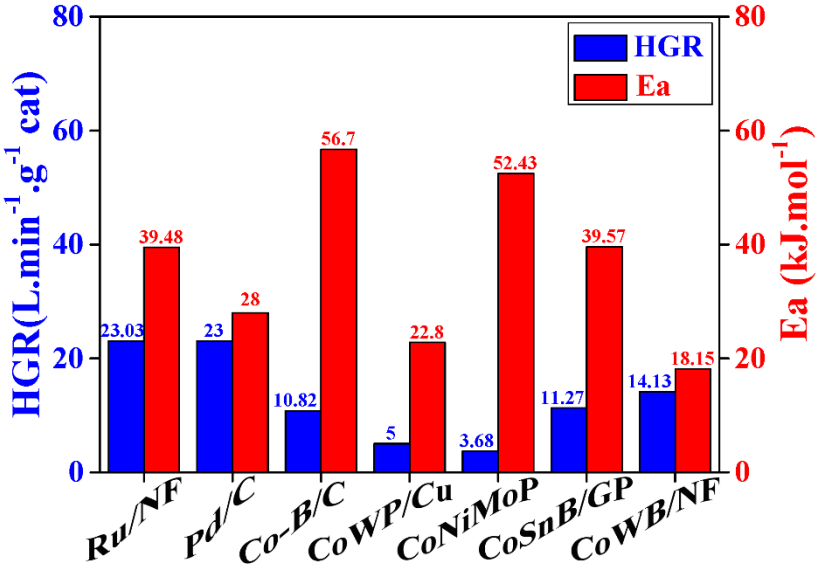

HGR
Ea
HGR(L.min-1.g-1 cat)
Ea (kJ.mol-1)
0
20
40
60
80
23.03
39.48
23
28
10.82
56.7
5
22.8
3.68
52.43
11.27
39.57
14.13
18.15
Ru/NF
Pd/C
Co-B/C
CoWP/Cu
CoNiMoP
CoSnB/GP
CoWB/NF

Figure 4

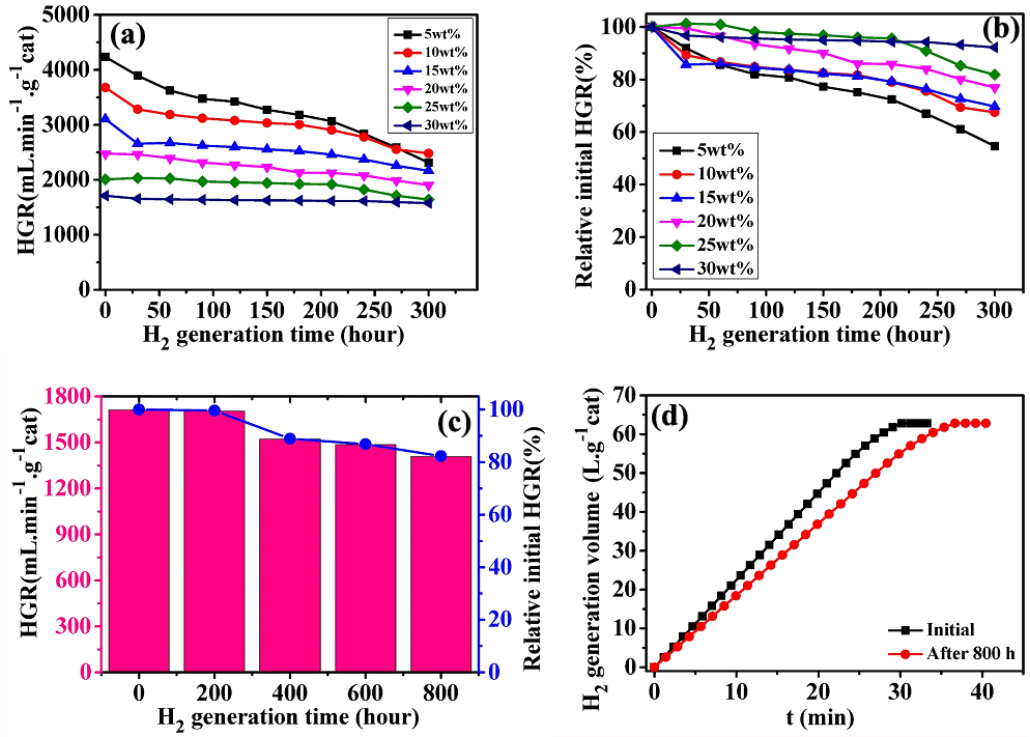

(a)
5wt%
10wt%
15wt%
20wt%
25wt%
30wt%
HGR(mL.min-1.g-1cat)
H2 generation time (hour)
(b)
Relative initial HGR(%)
H2 generation time (hour)
(c)
HGR(mL.min-1.g-1cat)
Relative initial HGR(%)
H2 generation time (hour)
(d)
H2 generation volume (L.g-1cat)
Initial
After 800 h
t (min)

Figure 5

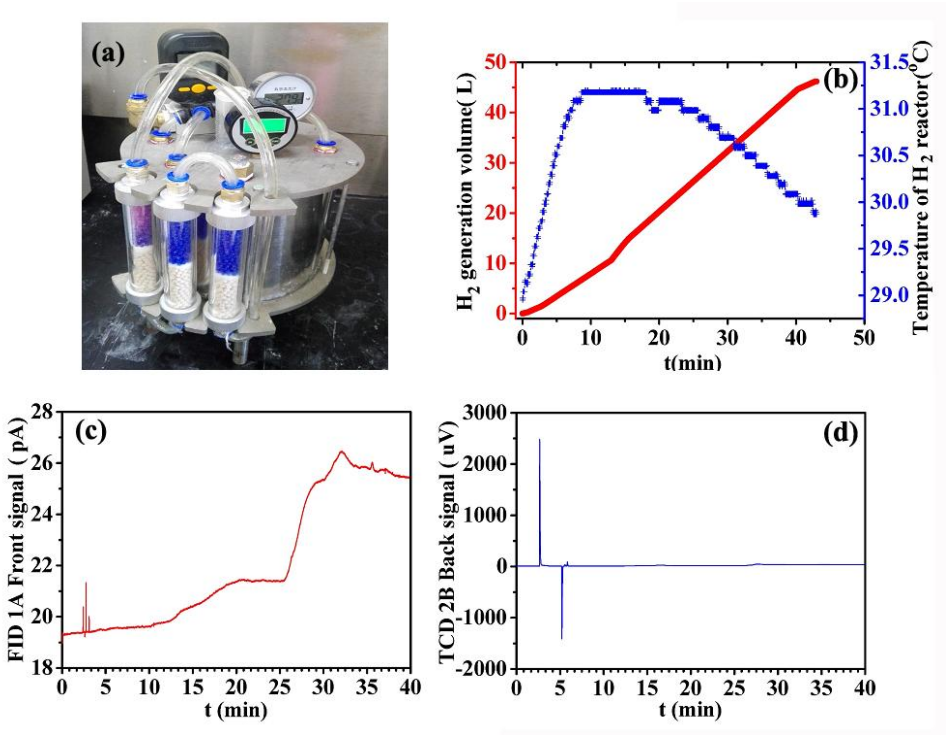

(a)
(b)
H_2 generation volume(L)
Temperature of H_2 reactor(°C)
t(min)
(c)
FID 1A Front signal (pA)
t (min)
(d)
TCD 2B Back signal (uV)
t (min)

Figure 6