Design and controlled synthesis of cobalt-loaded multi-walled carbon nanotube-magnetite nanocomposite as catalysts for hydrogen generation via hydrolysis of NaBH₄ under microwave heating

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ABSTRACT

Microwave (MW) irradiation is an attractive option for process intensification and has been proved effective in many catalytic processes. In this work, the (CNTs-Fe₃O₄)-Co nanocomposites were carefully design and successfully fabricated under a controlled manner. It was found that for the (CNTs-Fe₃O₄)$_{(1:4)}$-Co (10 wt%) catalyst, in the temperature range of 40 to 60℃, MW heating led to the hydrogen generation rate (HGR) being improved by 75 to 95.4% as compared with conventional heating. The synergistic effect of cobalt and Fe₃O₄ sites of the (CNTs-Fe₃O₄)$_{(1:4)}$-Co (10 wt%) catalyst was also verified by the evaluation of the catalytic performance of the (CNTs-Fe₃O₄) catalysts with different Co loading and DFT calculations. Moreover, the pre-exponential factor (A) of the NaBH₄ hydrolysis catalyzed by the (CNTs-Fe₃O₄)$_{(1:4)}$-Co (10 wt%) catalyst under MW heating was approximately 15 times higher than that of conventional heating, indicating that the effective collision frequency of the atoms at the reaction interface of the catalyst under MW heating was much higher than that of conventional heating because of the higher active sites on the surface of (CNTs-Fe₃O₄)$_{(1:4)}$-Co (10 wt%) catalyst under MW irradiation. Furthermore, the designed continuous experiment with microwave intermittent off-

on (5 min as a reaction cycle) was carried out at 26 ± 0.3℃ controlled by a continuous thermostatic water bath, and the results proved that both thermal and non-thermal effects of MW heating contributed to the enhancement of HGR under MW heating.

Keywords: Microwave-enhanced hydrolysis, non-thermal effect, sodium borohydride, (CNTs-Fe₃O₄)-Co catalysts, hydrogen generation.

1. INTRODUCTION

Hydrogen (H₂) is regarded as an attractive energy carrier in carbon-free energy systems [1]. By far, the most common commercial technique for H₂ generation is natural gas steam reforming and coal gasification followed by water-gas shift reaction, which are associated with significant CO₂ emissions [2]. In this regard, it is desirable to generate H₂ with no or less CO₂ emissions.

Sodium borohydride (NaBH₄) is a chemical hydride with several merits, such as high hydrogen content (10.8 wt%), non-toxic, non-flammable as well as regeneration nature [3] and is commonly used in hydrolysis to produce H₂ in the presence of catalysts under mild reaction temperature [4].

Microwave (MW) heating is of unique features such as volumetric heating, selective heating and high heating rate and has been utilized in liquid-phase reactions [5]. Specifically, in heterogeneous liquid-phase reactions, MW heating can promote selective heating, improve interfacial reaction and expedite mass transfer [6]. Accordingly, designing MW-responsive catalysts with the combination features of good MW absorbing ability and rich reactive sites is an effective approach for highly efficient reactions under MW heating. Although thermal effects and non-thermal effects of MW have been utilized to explain the mechanism of the MW-enhanced reactions [7], the existence of non-thermal effects is still a controversial debate and distinguishing the thermal and non-thermal effects of MW on the reaction mechanism by the experiments is still a challenge. Hence, it is necessary to design special experiments to verify the thermal and non-thermal effects of MW on the reaction mechanism.

It is speculated that MW heating might help enhance H2 generation rate in the hydrolysis of $NaBH_4$. Unfortunately, to date, a few attempts have been made to apply MW heating and MW-responsive catalysts simultaneously in the hydrolysis of $NaBH_4$ [8], and compared with conventional heating, the investigation focused on the increase in HGR of $NaBH_4$ hydrolysis under MW heating is still lacking. Consequently, it is desirable to design MW-responsive catalysts to investigate the increase in HGR of $NaBH_4$ hydrolysis under MW heating.

Carbon nanotubes (CNTs) is a promising supporting material of MW-responsive catalysts since it is an outstanding MW absorption material with high specific surface area and good thermal conductivity to be used as a support [21]. Normally, CNTs can promote the catalytic reactions by the formation of a large number of "hot spots" on the surface in heterogeneous aqueous reaction medium under MW irradiation [22], and also providing homogeneous and good dispersion of the as-fabricated catalysts [23, 24]. Likewise, magnetite (Fe_3O_4) has also been widely used as a potential supporting substance for MW-responsive catalysts due to its exceptional electromagnetic properties, suitable saturation magnetization, high curie temperature and cost-effective nature [25]. In addition, magnetic features of Fe_3O_4 are beneficial for the easy recovery of the spent catalysts by applying an external magnetic field in liquid phase reactions.

Non-precious metal nanoparticles, such as Co and Fe are commonly used to replace noble metals in $NaBH_4$ hydrolysis. Whereas agglomeration and low recyclability after hydrolysis are the two major disadvantages of the Co nanoparticles, which hinder its commercial utilization [9]. Hence, it is necessary to design a suitable supporting material to improve the dispersion as well as the recyclability of the catalyst.

Herein, cobalt-loaded multi-walled carbon nanotube-magnetite nanocomposite catalysts were designed and fabricated. Under the MW irradiation, the effects of the loading ratio of Co nanoparticles, the weight of the as-synthesized ($CNTs-Fe_3O_4$)-Co catalysts, the concentrations of NaOH and initial $NaBH_4$ as well as different heating methods (MW heating and conventional heating) on the catalytic activities of the hydrolysis of $NaBH_4$ were investigated. The existence of MW thermal and non-thermal effects in $NaBH_4$ hydrolysis was studied by the specially designed experiments.

2. MATERIAL AND METHODS

All chemicals utilized in this research, graphitized carboxylated multi-walled carbon nanotubes (99.9%), iron (III) acetylacetonate ($C_{15}H_{21}FeO_6$, 98%), absolute ethyl alcohol (C_2H_6O, $\geqslant$ 99.5%), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, AR, 99%) and sodium borohydride ($NaBH_4$, 98%), were purchased from Aladdin co ltd. All chemicals used without any further purification.
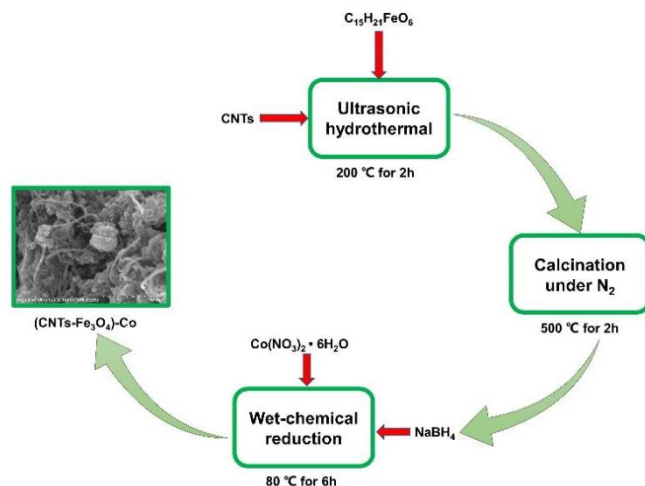

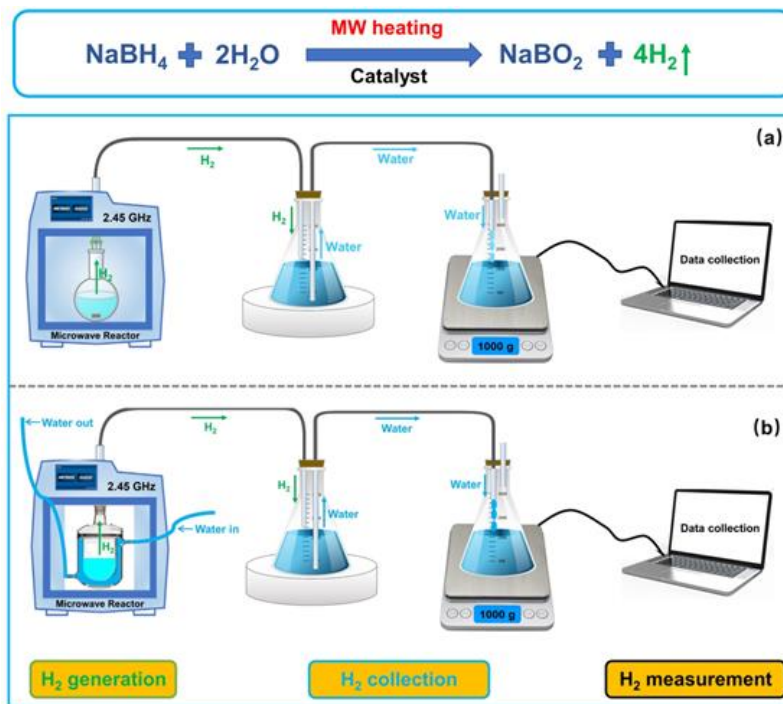Fig. 1. Schematic representation of the fabrication of the ($CNTs-Fe_3O_4$)-Co catalysts

Fig. 2. Schematic of experimental set-up for the study of MW-enhanced catalytic hydrolysis of $NaBH_4$

3.   RESULTS AND DISCUSSION

3.1   The synergistic catalytic effect of Co and Fe_3O_4

The synergistic catalytic effect of Co and Fe_3O_4 of $(CNTs-Fe_3O_4)_{(1:4)}$-Co (10 wt%) catalyst was verified by investigating the catalytic activity of the samples under the optimized experimental conditions. The experimental results as shown in Fig. 3 (a) and (b). It can be seen from Fig. 3 (a) that the total H_2 generation volume within 20 min of the pure CNTs and pristine Fe_3O_4 was only 313 mL and 393 mL respectively, which was just a little bit higher in comparison to the reaction system without catalyst (286 mL). However, the overall H_2 yield of the as-prepared CNTs-Co (10 wt%), $(CNTs-Fe_3O_4)_{(1:4)}$ composite and $(CNTs-Fe_3O_4)_{(1:4)}$-Co (10 wt%) increased rapidly to 583 mL, 1127 mL and 1688 mL, respectively. Besides, as shown in Fig. 3 (b), the HGR of the $(CNTs-Fe_3O_4)_{(1:4)}$-Co (10 wt%) was approximately 2.1 folds and 4.4 folds higher than that of $(CNTs-Fe_3O_4)_{(1:4)}$ composites and CNTs-Co (10 wt%), which was 1664, 802 and 379 mL g-1 min-1, respectively. Accordingly, the catalytic performance of the $(CNTs-Fe_3O_4)_{(1:4)}$-Co (10 wt%) composite was due to the synergistic effect of Co sites and Fe_3O_4 sites. The synergistic mechanism was that the electron rich center (Fe^{2+}, Co^0 and Co^{2+}) and electron deficient center (Fe^{3+} and Co^{3+}) of the $(CNTs-Fe_3O_4)_{(1:4)}$-Co (10 wt%) catalyst can be the activation center of BH4- and

H_2O, respectively, which is beneficial for the relative high HGR of the $(CNTs-Fe_3O_4)_{(1:4)}$-Co (10 wt%) catalyst [10].

Furthermore, the synergistic characteristics between Co and Fe_3O_4 were also investigated by the computational calculations. From the HRTEM images, the observed Co (002) is rare. Co atoms was highly dispersed as indicated in the XRD analysis and EDX mapping results. It can be speculated that most Co atoms were in the form of clusters. From XPS results, the number of Co^0 is smaller than that of Co^{2+} and Co^{3+}, which indicated that most Co atoms entered the Fe_3O_4 and replaced the surface Fe^{3+} and Fe^{2+} atoms or were oxidized by surface oxygen atoms. In addition, as the Co (002) was observed on the Fe_3O_4 (110) surface, the Fe_3O_4(110) surface was selected as the substrate. Subsequently, the models of Co cluster with 5 Co atoms [11] and Co substituted Fe_3O_4(110) supported Co cluster where the dissociation of BH4- took place were built as shown in Fig. 3 (c). The corresponding free energy diagram was depicted in Fig. 3 (d).

It can be seen that the rate-determining step was the breakage of the last B-H bond. According to previous studies [11], the reaction will occur in the center of three Co atoms. Compared with the pristine Co5 cluster with one kind of active site, the Co substituted Fe_3O_4(110) supported Co5 cluster exhibited four possible reaction sites. The most stable adsorption site was the D site with least total energy after BH4 adsorption (Fig. 3 (c)-Top

view). Two Co atoms originating from Co5 cluster in the D site bond with surface O, indicating a lower oxidizing state Co^{2+}. Another Co atom was the substitution of surface Fe^{3+}, which implied that this Co atom can be the Co^{3+} ion. Compared with the Co5 with Co0 atoms, the D site from the Co substituted Fe_3O_4(110) supported Co5 cluster with Co^{2+} and Co^{3+} showed a rate-determining step reaction free energy of 0.47 eV which was lower than that on Co5 cluster with 0.67 eV. Obviously, the catalytic efficiency of $NaBH_4$ for H_2 production will be highly improved, which can be attributed to the synergistic catalytic effect of Co and Fe_3O_4.
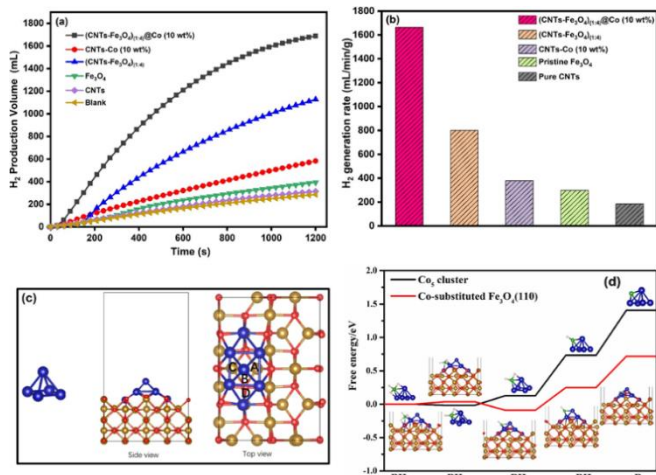

Fig. 3. **(a)** The overall H_2 generation kinetics curves of the samples; **(b)** The corresponding HGR of (a). **(c)** Pristine Co5 cluster, Side and top view of Co-substituted Fe_3O_4(110) supported Co5 cluster; **(d)** The free energy diagram of H dissociation steps on the pristine Co5 cluster and the D site (Fig. 3 (c)-Top view) from Co substituted Fe_3O_4(110) surface (The gold, red, blue, green and pink balls referred to Fe, O, Co, B and H atoms, respectively).

3.2 The thermal effects of MW irradiation

To evaluate the thermal effects of MW irradiation on the catalytic performance of $NaBH_4$ hydrolysis, a series of experiments both under MW heating and conventional heating at each reaction temperature, ranging from 40 to 60℃, were conducted and the corresponding HGR of the (CNTs-Fe_3O_4)$_{(1:4)}$-Co (10 wt%)/ $NaBH_4$ hydrolysis system was analyzed.

As shown in Fig. 4 (f), it was obvious that the HGR of the (CNTs-Fe_3O_4)$_{(1:4)}$-Co (10 wt%) catalyst increased dramatically with the increase in reaction temperature, indicating that higher temperature has obvious positive effect on $NaBH_4$ hydrolysis. Moreover, the HGR was always higher under MW heating than that of conventional heating. In detailed, compared to the HGR

of conventional heating, the enhancement ratio of HGR under MW irradiation showed an increase trend with the increase in reaction temperature from 40 to 60℃.

These observed accelerations in H_2 generation under MW heating were mainly ascribed to the presence of MW selective heating of the (CNTs-Fe_3O_4)$_{(1:4)}$-Co (10 wt%) catalyst, forming hot spots at the surface of the (CNTs-Fe3O4)(1:4)-Co (10 wt%) catalyst in the heterogeneous liquid-solid reaction systems. The generated hot spots can create a large number of high-temperature micro-domains, in which the temperatures were 100 -150K higher than that of the remainder of the liquid-solid reaction systems [12]. Hence, when the BH_4^- and H_2O molecules in the MW/(CNTs-Fe_3O_4)$_{(1:4)}$-Co (10 wt%)/ $NaBH_4$ hydrolysis system absorbed on the surface of the(CNTs-Fe_3O_4)$_{(1:4)}$-Co (10 wt%) catalyst, the H_2 would be generated rapidly within or near those hot spots, resulting in the increase in the HGR as compared with conventional heating [12]. Furthermore, the heating rate of $NaBH_4$ hydrolysis in the MW/ (CNTs-Fe_3O_4)$_{(1:4)}$-Co (10 wt%)/ $NaBH_4$ hydrolysis system can also increase faster in comparison to conventional heating due to the liquid-solid reaction systems can be heated by both ionic conduction ((CNTs-Fe_3O_4)$_{(1:4)}$-Co (10 wt%)) and dipole polarization (H_2O) [13], which also have positive effects on the efficiency of H_2 generation of NaBH4 hydrolysis [14].
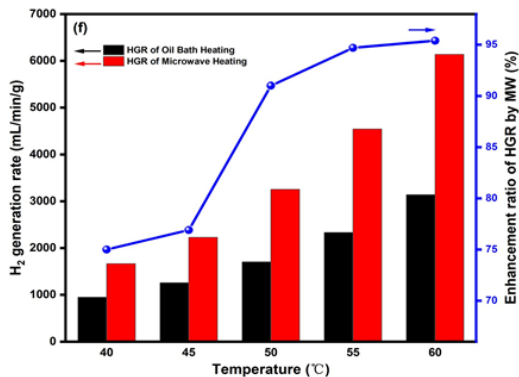

Fig. 4. Comparison of HGR at each reaction temperature under MW heating and conventional heating.

3.3 The non-thermal effects of MW irradiation

Apart from the thermal effect of MW, the non-thermal effect of MW also contributed to the enhancement in catalytic performance when the ((CNTs-Fe_3O_4)$_{(1:4)}$-Co (10 wt%) catalyst was applied in $NaBH_4$ hydrolysis under MW irradiation. The differences in activation energy (Ea), pre-exponential factor (A) was analyzed under MW heating and conventional heating.

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It can be seen that the A under MW irradiation was much higher (approximately 15 times) than that of conventional heating. The higher A indicated that the effective collision frequency of the atoms at the reaction interface of the $(CNTs-Fe_3O_4)_{(1:4)}$-Co (10 wt%) catalyst under MW heating was much higher than that of conventional heating, resulting in the significantly higher reaction rate of the as-fabricated catalyst under MW-enhanced catalytic reaction [15]. This was ascribed to the occurrence of the non-thermal effect when the aqueous reaction system under MW irradiation [14]. In detailed, the non-thermal effect of MW irradiation can induce the improvement of the diffusion rate of reactant molecules and atoms, such as BH4, BH3, BH2, BH, H^+ and OH^-, at the reaction interface in several reaction steps. Furthermore, the chemical bond of a polar reactant molecule (eg. H_2O) can be weakened due to its higher frequency of agitation and mobility under MW irradiation [14]. Thus, H^+ generated from H_2O, which was the rate-determining step of $NaBH_4$ hydrolysis, would be easier, resulting in the increase in the frequencies and quantities of H_2 formation via the combination of hydridic hydrogen atoms from $NaBH_4$ ($Na^+BH_3H^-$) with acidic hydrogen atoms of H_2O (H^+OH^-) [16].

Furthermore, to further prove the occurrence of non-thermal effect as well as its effect on $NaBH_4$ hydrolysis process using the $(CNTs-Fe_3O_4)_{(1:4)}$-Co (10 wt%) as catalyst under MW irradiation, the special continuous experiment with 5min as a cycle of MW intermittent turn off-on was designed (Fig. 2 (b)). The designed special experimental set-up was carried out at $26\,℃ \pm 0.3\,℃$ controlled by the continuous high-speed water flow, which minimize the thermal effects of MW caused by the rise in temperature.

The result of the overall H_2 generation volume curves are shown as Fig. 5 (e). It indicated that the catalytic reaction process route of $NaBH_4$ hydrolysis was obviously altered by intermittent turning off-on (5 min as a cycle) MW during the catalytic reaction process. When compared with the result curve of the whole catalytic reaction process without MW irradiation, the overall H_2 generation volume of MW intermittent turn off-on was higher within the same reaction time and periods. Moreover, as the hydrolysis reaction processing, the concentration of $NaBH_4$ (C_{NaBH4}) continued to decline both under MW turn off-on and without MW irradiation conditions. However, the C_{NaBH4} of MW turn off-on is clearly lower than that of without MW irradiation at the identical reaction point. Specifically, at the reaction point of 3000 s, the remained C_{NaBH4} of MW turn off-on is 19.5%, which is much lower than that of without MW irradiation (32.5%). This indicated that more $NaBH_4$ was hydrolyzed due to the MW off-on condition.

Additionally, Fig. 5 (f) shows the real time HGR of MW intermittent off-on control (Red-Gray symbol-line) and without MW irradiation (wathet blue symbol-line) within 3000 s. It can be seen obviously that the real time HGR under MW turn on period all trended up continuously, and once MW was turned off, the real time HGR always showed a continuous decreased trend. However, the real time HGR corresponded to the whole $NaBH_4$ hydrolysis without MW irradiation decreased continuously as the reaction progresses. Furthermore, within 3000 s of reaction time, most of the real time HGR of without MW irradiation is lower than that of under MW off-on because the MW non-thermal effect and relatively high C_{NaBH4} played a dominant role in hydrolytic reaction at this reaction period. Nevertheless, as shown in Fig. S2, after 3000 s of the reaction time, although the non-thermal effect of MW still can improve HGR under MW turn on period, most of the real time HGR of MW off-on is, in turn, lower than that of without MW irradiation because the much lower C_{NaBH4} in MW off-on reaction system cannot contribute to the higher HGR in the rest of the hydrolytic reaction in comparison to the reaction system without MW irradiation.

Accordingly, the abovementioned results validated the occurrence of the non-thermal MW effect and its positive effect on $NaBH_4$ hydrolysis.
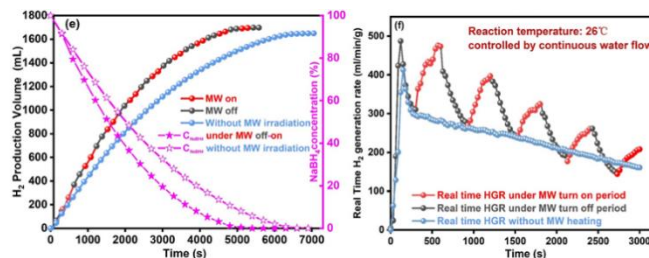

Fig. 5. (e) Comparison of the overall H_2 generation kinetics curves and real time C_{NaBH4} of MW intermittent switch off-on control (Red-Gray symbol-line) and without MW irradiation (wathet blue symbol-line) at $26 \pm 0.3\,℃$; (f) Real time HGR of MW intermittent switch off-on control (Red-Gray symbol-line) and without MW irradiation (wathet blue symbol-line) within 3000 seconds.

4. CONCLUSION

Herein, a series of microwave-responsive catalysts $(CNTs-Fe_3O_4)$-Co were designed and synthesized successfully. MW heating can significantly improve the catalytic activity of the $(CNTs-Fe_3O_4)_{(1:4)}$-Co (10 wt%). Compared with conventional heating, the HGR of the $(CNTs-Fe_3O_4)_{(1:4)}$-Co (10 wt%) for $NaBH_4$ hydrolysis under MW heating increased from 75 (40℃) to 95.4% (60℃).

The synergistic catalytic effect between Co and Fe_3O_4, which was verified by experiments and DFT calculations, lead to the good HGR of the $(CNTs-Fe_3O_4)_{(1:4)}$-Co (10 wt%), indicating that the $(CNTs-Fe_3O_4)_{(1:4)}$-Co (10 wt%) was approximately 2.1 folds and 4.4 folds more active than that of $(CNTs-Fe_3O_4)_{(1:4)}$ composites as well as CNTs-Co (10 wt%), respectively, and the Fe_3O_4(110) supported Co5 cluster showed a rate-determining step reaction free energy of 0.47 eV which was lower than that on pure Co5 cluster with 0.67 eV. Furthermore, the pre-exponential factor of the MW/ $(CNTs-Fe_3O_4)_{(1:4)}$-Co (10 wt%)/ $NaBH_4$ hydrolysis system under MW heating was approximately 15 times higher than that of conventional heating, indicating that the effective collision frequency of the atoms at the reaction interface of the $(CNTs-Fe_3O_4)_{(1:4)}$-Co (10 wt%) catalyst under MW heating was much higher than that of conventional heating. The existence of the non-thermal effect of MW has been proved by the special designed experimental set-up. Also, both thermal and non-thermal effects of MW irradiation contributed to the enhancement of the HGR in $NaBH_4$ hydrolysis.

ACKNOWLEDGEMENT

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