Preparation of magnetically recyclable CuFe₂O₄/RGO for catalytic hydrolysis of sodium borohydride

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Abstract

CuFe₂O₄/reduced graphene oxide (RGO) nanostructures were fabricated by a facile chemical method, and the shape and size of the CuFe₂O₄ nanoparticles were tuned through changing the concentration of the reactants and the reaction temperature. The CuFe₂O₄/RGO nanostructures were firstly analyzed by transmission electron microscopy, Fourier Transform infrared spectroscopy and powder X-ray diffraction, and then they were exploited as magnetically recyclable catalyst for the hydrolytic dehydrogenation of NaBH₄ for hydrogen evolution. They exhibited superior catalytic activity and recyclability. The calculated activation energy was 33.95 kJ mol⁻¹, which is even lower than some metallic nanoparticle catalysts. So the CuFe₂O₄/RGO nanostructures will find potential applications as magnetically recyclable catalysts in hydrogen storage system for fuel cell applications.

Key words: CuFe₂O₄/RGO, nanostructure, NaBH₄, hydrolytic dehydrogenation, hydrogen

1. Introduction

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Recently, the excessive exploitation of fossil fuels and the ever growing demand for energy have greatly inspired the seeking for new clean energies [1-3]. Due to the ideal characteristics of combustion efficiency, high energy density, and non-toxic harmless, hydrogen gas has become one of the most attractive energy in many energy carriers [4, 5]. In addition, as we all known, hydrogen is usually stored in the form of inorganic hydride and hydrocarbon compounds in nature, so electrolyzing of water, ethanol steam, hydrolyzing of boron hydride to produce hydrogen gas and so on has become commonly used methods [6-8]. In all kinds of hydrogen storage materials, sodium borohydride (NaBH_4) and ammonia borane are considered as ideal hydrogen storage materials due to their highly favorable hydrogen storage, extensive source and suitable hydrogen production rate at low temperature. Therefore, hydrolytic dehydrogenation of NaBH_4 is considered to be the most convenient approach for H_2 production. However, though the reaction of NaBH_4 hydrolysis is spontaneous, the rate is quite slow, so choosing appropriate catalysts to speed up the reaction is considered crucial and attractive. In recent years, lots of potential catalysts have been reported in the literatures, such as Pt, Ru, Co and metallic alloy nanoparticles [9-13].

Non-noble Cu nanoparticles are cheap and easy fabrication compared to traditional catalysts [14, 15]. They displayed high activity in catalytically synthesizing diaryl ethers, aryl and vinyl dithiocarbamates in a satisfactory yield via Ullmann-type coupling and condensation. The catalytic performance of Cu nanoparticles depends on their size and dispersion [16-18], so using supporter or integrating with other metals has been demonstrated to be effective ways to enhance their catalytic performance [19-21]. Cu nanoparticles supported on TiO_2 nanofibers were an effective photocatalyst for hydrolytic dehydrogenation of ammonia borane under solar radiation [22]. The results reveal that high rate of hydrogen was released from

ammonia borane as compared with undecorated TiO₂ nanofibers and pristine Cu NPs. Cu@FeCo core-shell nanoparticles containing Cu cores and FeCo shells exerted composition-dependent activities towards the catalytic hydrolysis of ammonia borane [23].

Graphene has a monolayer structure that contains carbon atoms tightly packed into two-dimensional honeycomb lattices [24]. Since it was reported in 2004 [25], graphene has attracted a great deal of attention for its potential applications in catalyst supports, nanoelectronic devices, energy, composite materials, and biological detection devices [26-30]. Because it has large surface area and large amounts of oxygen-containing functional group, graphene oxide (GO, oxidized graphene) has become one of the most ideal substrates to grow metal and metal oxide nanoparticles and maintain the stability of these nanoparticles during their usage [31].

Nanoparticles have large surface area and high density of surface active sites, so they usually exhibit excellent catalytic performance as catalysts. However, they also have some shortcomings, such as easy agglomeration and difficulty in removing them from the solution, which restricts their practical applications. In order to solve the problems, some approaches have been developed. Using supporter is an effective way to prevent agglomeration while magnetic modification can realize magnetically separating. Magnetically recyclable Fe₃O₄@C@Ag, Ag-coated Fe₃O₄@TiO₂ and Pt-Ru/Fe₃O₄/C for photocatalytic and chemical reactions have been developed [32-34]. Fe₃O₄@Ag nanocomposites showed outstanding catalytic activity, convenient magnetic separability, and long-term stability for the degradation of Rhodamine B and neutral red [35, 36].

In this paper, CuFe₂O₄/RGO nanostructures with various RGO contents were synthesized by using the hydrothermal process, and the factors that affect the shape

and size of the attached CuFe_2O_4 nanoparticles were studied. The graphene acts as a supporter to prohibit agglomeration of CuFe_2O_4 nanoparticles. CuFe_2O_4 nanoparticle itself is magnetic and responses to external magnetic field, so it is easy to collect them by applying an external magnetic field with a magnet. At the same time, CuFe_2O_4 nanoparticles contain Cu element that is expected to have catalytic ability for hydrolytic dehydrogenation of NaBH_4 . So $\text{CuFe}_2\text{O}_4/\text{RGO}$ is both magnetically separable and catalytically active. The catalytic performance of $\text{CuFe}_2\text{O}_4/\text{RGO}$ for hydrolytic dehydrogenation of NaBH_4 for hydrogen evolution was investigated. The hydrogen generation rate reached $622 \text{ (mL min}^{-1} \text{ g}^{-1}\text{)}$, and the yields remained almost 100 % after six rounds of reaction. It demonstrates that $\text{CuFe}_2\text{O}_4/\text{rGO}$ nanostructures are recyclable catalysts in practical applications.

2. Experimental

2.1 Materials

Graphite came from Qingdao Graphite Factory. NaNO_3 , KMnO_4 , H_2O_2 (30%), $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$, H_2SO_4 , polyvinylpyrrolidone (PVP), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, ethylene glycol (EG), CH_3COONa etc reagents were purchased from Tianjin Chemical Reagent Co. All the above chemicals were used as received.

2.2 Preparation of $\text{CuFe}_2\text{O}_4/\text{RGO}$ Nanostructures

GO was prepared by a modified Hummers method from purified natural graphite [31]. The detail procedure for synthesizing $\text{CuFe}_2\text{O}_4/\text{RGO}$ nanostructures by a hydrothermal method is as follow: GO (25 mg) was ultrasonicated in a 50 mL mixture solution of EG and distilled water for 1.5 h to form a suspension. Then 0.1 mmol $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.2 mmol $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were added into the suspension and ultrasonicated for 20 min. After that, 6 mmol CH_3COONa and 0.05 g PVP were added and stirred for 20 min. The mixture was transferred to a Teflon-lined stainless

steel autoclave and maintained at 180 °C for 10 h, and then put in air to cool down to room temperature. The black product was rinsed with distilled water and ethanol for several times, and then dried at 40 °C in a vacuum oven to gain the CuFe₂O₄/RGO nanostructures.

2.4 Characterization

The X-ray diffraction (XRD) patterns of the CuFe₂O₄/RGO nanostructures were taken using an x-ray diffractometer (BDX3300) with a reference target, Cu K α radiation ($\lambda=0.154\text{nm}$) voltage, 30 kV, and current, 30 mA. A step of 4°/min was chosen to measure samples from 10° to 90°. The sample for transmission electron microscopy (TEM) was prepared by placing drops of a diluted CuFe₂O₄/RGO suspension onto carbon coated Ni grid and then dried under ambient condition prior to being introduced into the TEM chamber. Fourier transform infrared (FTIR) spectra of the CuFe₂O₄/RGO nanostructures were recorded with a Perkin-Elmer Paragon-1000 FTIR spectrometer in the range of 500-4000 cm⁻¹, and each FTIR spectrum was the average of 20 scans. Thermogravimetric analysis was performed in the air atmosphere on a Rigaku-TD-TDA analyzer with a heating rate of 5 °C/ min. An X-ray photoelectron spectrometer (XPS, PHI1600 ESCA System, PERKIN ELMER, US) was employed to analyze elements in the CuFe₂O₄/RGO nanostructures. The composition was also measured by an inductively coupled plasma optical emission spectrophotometer (ICP-OES, Vista-MPX, Varian).

2.5 Catalytic experiments

The reaction of hydrogen generation by hydrolysing of NaBH₄ was conducted in a batch system equipped with a thermometer. At first, 30 mg CuFe₂O₄/RGO was placed into a three-necked round-bottom. Then, 20 mL alkaline NaBH₄ solution (containing 22.5, 33.8 or 45.0 mmol/L) in a 50 mL constant pressure funnel was added to the

bottom of the three-necked round-bottom. The volume of the generated H_2 was measured by monitoring the water displacement from the inverted measuring cylinder as the hydrolysis proceeded. When the reaction finished, the $CuFe_2O_4/RGO$ was easily removed from reaction solution with a magnet. It was rinsed with distilled water for several times before it was reused in the next round of $NaBH_4$ hydrolysis. The $CuFe_2O_4/RGO$ was applied for six successive runs to investigate its recyclability. To determine the impact of reaction temperature on the hydrolysis reaction, the hydrolysis proceeded at different temperatures.

3. Results and discussion

Hydrothermal synthesis is an available way to prepare nanoparticles because it can adjust particle size, shape and architecture by adding additives or changing reaction conditions. The formation mechanism for $CuFe_2O_4/RGO$ by hydrothermal method is illustrated in Figure 1. The GO sheets have functional groups that can attract the metal ions that produce $CuFe_2O_4$ nanoparticles during hydrothermal process, and GO itself is reduced at the same time.

Figure 1 Schematic illustration for the formation mechanism of $CuFe_2O_4/rGO$

In order to obtain the best reaction conditions for CuFe₂O₄/RGO preparation, the impacts of the reaction temperature, the mass ratio of GO to metal precursors and the reaction time on the morphology of the CuFe₂O₄/RGO were investigated. Figure 2 shows the TEM images of CuFe₂O₄/RGO nanostructures made at different reaction temperatures. As shown in Figure 2A-B, the CuFe₂O₄ nanoparticles prepared at 130 °C are very small (about 5 nm) but they are seriously aggregated, so it is difficult to identify a single nanoparticle. When the temperature rose to 180 °C, CuFe₂O₄ nanoparticles on the RGO nanosheets were more regular in shape however their size increased to about 100 nm (Figure 2C). In addition, the crystal lattices were clearly observed in Figure 2D. Thus, the regular and crystalline CuFe₂O₄ nanoparticles can be formed on RGO nanosheets at higher temperature.

Figure 2 TEM images of $\text{CuFe}_2\text{O}_4/\text{RGO}$ prepared at different reaction temperatures:

(A, B) 130 °C, (C, D) 180 °C.

Next, the effect of RGO ($m_{\text{GO}}/m_{\text{Fe-Cu}}$: 2.84, 1.42, 0.95) on the CuFe_2O_4 morphology was investigated and the TEM images of these $\text{CuFe}_2\text{O}_4/\text{RGO}$ nanostructures are shown in Figure 3. At $m_{\text{GO}}/m_{\text{Fe-Cu}}=2.84$, the CuFe_2O_4 nanoparticles were evenly distributed on the RGO sheets, and their average size was about 100 nm (Figures 3A-B). When the $m_{\text{GO}}/m_{\text{Fe-Cu}}$ was decreased to 1.42, a large number of fusiform CuFe_2O_4 particles with diameters of about 130 nm were observed (Figures 3C-D). More interestingly, when the $m_{\text{GO}}/m_{\text{Fe-Cu}}$ was further decreased to 0.95, the shape of the CuFe_2O_4 particles changed from fusiform to cuboid, or trunked fusiform, and the size of the particles became even bigger, about 160 nm (Figures 3E-F). The results demonstrate that GO takes a crucial role in tuning both the shape and size of the CuFe_2O_4 nanoparticles. In addition, in the CuFe_2O_4 surface, a lot of bright spots (Figure 3G) appeared, this indicates that the fusiform and cuboid may be constituted from self-assembly of even small nanoparticles in the hydrothermal process. The magnified image in Figure 3H clearly shows parallel lines of crystal lattices. The

lattice spacing between the two adjacent planes was measured to be approximately 0.25 nm which indexes to the (202) lattice planes of cubic spinel ferrite structure [37].

Figure 3 TEM images of CuFe₂O₄/RGO prepared with different m_{GO}/m_{Fe-Cu} ratios: 2.84 (A and B), 1.42 (C and D), 0.95 (E and F), and the HRTEM of CuFe₂O₄/RGO prepared with m_{GO}/m_{Fe-Cu} of 1.42 (G and H).

In order to determine the formation process of the CuFe₂O₄/RGO, CuFe₂O₄/RGO nanostructures formed in different reaction time were observed. Figure 4 shows the TEM images of the CuFe₂O₄/RGO prepared in 6, 12, and 24 h. After 6 h of reaction, there were many CuFe₂O₄ particles supported on the RGO nanosheets (Figure 4A), and they are fusiform particles with diameters of about 80 nm (Figure 4B). After extra 6 h of reaction, no obvious change in shape was observed except the size became big, 130 nm (Figure 4C-D). When the reaction time extended to 24 h, the CuFe₂O₄ became small (60 nm) and looked rough on surface. It seems that the CuFe₂O₄ particles are consisted of many even smaller nanoparticles. The EDX result in Figure 4G indicates the presence of Fe, Cu, C and O (the Ni is from the Ni grid as a sample supporter) and the Fe/Cu atomic ratio of 1.96/1. TEM and EDX results demonstrate the formation of RGO supported CuFe₂O₄ nanoparticles.

Figure 4 TEM images of $\text{CuFe}_2\text{O}_4/\text{RGO}$ prepared at different reaction times: (A and B) 6 h, (C and D) 12 h, and (E and F) 24 h; EDX spectrum of the $\text{CuFe}_2\text{O}_4/\text{RGO}$ (G)

Figure 5A gives the FTIR spectra of $\text{CuFe}_2\text{O}_4/\text{RGO}$ and GO. GO has two strong peaks at 3400 cm^{-1} (O–H stretching vibrations) and 1617 cm^{-1} (skeletal vibrations from graphitic domains) [38]. The former is attributed to the adsorbed water and –OH groups on the GO and the latter to the aromatic rings of the graphitic sheets. The GO also has a peak at 1738 cm^{-1} ($\nu_{\text{C=O}}$) which is attributed to the carbonyl and carboxylic groups [38]. However, this peak is not present in $\text{CuFe}_2\text{O}_4/\text{RGO}$, which proves that the C=O groups have been removed. So GO has been reduced in the process of $\text{CuFe}_2\text{O}_4/\text{RGO}$ preparation. In addition, in $\text{CuFe}_2\text{O}_4/\text{RGO}$, there are two peaks at 556 and 459 cm^{-1} which corresponding to the peak in CuFe_2O_4 [39]. The above results demonstrate the formation of $\text{CuFe}_2\text{O}_4/\text{RGO}$ nanostructures.

Figures 5B and C show the XRD pattern of the $\text{CuFe}_2\text{O}_4/\text{RGO}$ and RGO. It can be seen that the main peaks at 33.31° , 35.42° , 43.14° , 50.14° , 54.32° , 62.51° and 74.2° correspond to the (220), (311), (400), (422), (511), (440), and (533) crystal planes of cubic spinel CuFe_2O_4 (JCPDS 01-077-0010) [40]. RGO only has a small peak at

about 22.5°. It is too weak to be observed in CuFe₂O₄/RGO. This further confirms that CuFe₂O₄ on RGO is crystalline.

Figure 5 FTIR spectra of GO and CuFe₂O₄/RGO(A), and XRD diagram of CuFe₂O₄/RGO (B) and RGO (C).

TGA analysis is a useful tool to study thermal stability of materials and determine composite composition. The TGA curves of CuFe₂O₄ and CuFe₂O₄/RGO nanostructures in air atmosphere were measured and shown in Figure 6. It demonstrates that CuFe₂O₄ particles are stable. The CuFe₂O₄/RGO has two mass losses at around 400 and 650°C respectively, which can be assigned to the degradation of RGO and PVP and oxidation of C. According to the weight losses of CuFe₂O₄ and CuFe₂O₄/RGO, the amount of CuFe₂O₄ in the CuFe₂O₄/RGO is estimated to be about 45.0 wt %, which is confirmed by ICP analysis.

Figure 6 TGA curves of CuFe₂O₄/RGO and CuFe₂O₄.

XPS is a useful method to determine elemental valences, composition and functional groups of compounds. The XPS survey spectrum in Figure 7A indicates the existence of Fe, Cu, O, and C elements that come from CuFe₂O₄ and RGO. The atomic ratio of Cu to Fe is about 1:2.19, that approximately agrees with the theoretic ratio. In the Cu 2p spectrum (Figure. 7B), the two peaks at 933.6 eV and 954.1 eV are assigned to 2p_{1/2} and 2p_{3/2} of the metallic Cu²⁺ state respectively [41]. In the Fe 2p XPS spectrum (Figure 7C), the peaks at 721.9 and 711.5 eV correspond to 2p_{1/2} and 2p_{3/2} of the metallic Fe³⁺ state respectively. Figure 7D shows the deconvoluted XPS spectrum for C1s. The peaks at 284.6 eV, 286.42 and 288.09 are assigned to C=C, C-OH and C-O-C bonds, respectively. The peak area ratios of C-OH/C=C and C-O-C/C=C are 0.15 and 0.07 (for GO, they are 0.82 and 0.10 respectively), indicating that the number of oxygen-containing groups in the CuFe₂O₄/rGO decreases significantly, so GO has been reduced. All these results further confirm the formation of CuFe₂O₄/RGO.

Figure 7 XPS survey spectrum of CuFe₂O₄/RGO (A); the Cu 2p and Fe2p core level spectra (B, C), deconvoluted XPS spectrum for C1s (D).

The hydrogen generation from hydrolysis of NaBH₄ was used as a model reaction to assess the catalytic performance of the CuFe₂O₄/RGO. Figure 8A shows the volume of hydrogen generated in the catalytic hydrolysis of NaBH₄ solution in the presence or absent of the CuFe₂O₄/RGO. The hydrolytic rate of NaBH₄ is very slow, but it remarkably increases when the reaction is catalyzed by the CuFe₂O₄/RGO. The hydrolysis of NaBH₄ was rapidly completed in the presence of small amount of catalyst. The hydrolysis of 40 mg NaBH₄ was completed within 40 min in the presence of 30 mg catalyst (3.6 mg Cu determined by ICP) and released 89.6mL hydrogen gas, which corresponds to the rate of 622 (mL min⁻¹ g⁻¹). This value is lower than some noble metal particles (Pt, Ru) shown in the Table 1, but is higher than Ni-Ru, Au, Ni and Cu particles.

Figure 8 Plot of hydrogen volume versus reaction time in the NaBH₄

hydrolysis catalyzed by CuFe₂O₄/RGO (3.6 mg CuFe₂O₄)

Table 1 Comparison of hydrogen generation rate of the CuFe₂O₄/rGO with other reported catalysts

Catalysts	Rate (mL min ⁻¹ g ⁻¹)	References
Pt/LiCoO ₂	2700	42
Ru/LiCoO ₂	3000	42
PVP-protected Au	274	43
PVP-protected Ni	777	43
Ni-Ru	400	44
Co–Ni–P/Pd-TiO ₂	460	45
p(HEMA)-Co	1734	46
p(HEMA)-Ni	478	46
p(HEMA)-Cu	29	46
p(2-VP) ⁺ -Ni	140	47
p(2-VP) ⁺ -Cu	75.8	47
Co ₃ O ₄	980	48
Co	490	48
present	622	

The effect of NaBH₄ concentration on hydrogen generation was studied by doing a series of experiments with varying initial concentration of NaBH₄ while

keeping the other conditions unchanged. Figure 9A shows the generated hydrogen in these reactions. It is obvious that high NaBH_4 concentration produces more hydrogen but need more time to complete the reaction. However, the reaction rates in the initial stage are nearly identical. So changing NaBH_4 concentration is an efficient way to control hydrogen yield and hydrogen generation rate.

Since the supporter takes an important role in the generation of hydrogen by NaBH_4 hydrolysis, the impact of RGO on the catalytic activity of the $\text{CuFe}_2\text{O}_4/\text{RGO}$ nanostructures was also investigated. Here, three samples prepared by different GO content were used as catalysts for NaBH_4 hydrolysis, and the volume of generated hydrogen gas versus time is shown in Figure 9B. It can be seen that the hydrogen generation rate decreased with increasing RGO amount. From the perspective of saving time, low RGO amount is favorable because more hydrogen releases in short time with high rate.

Figure 9 Effects of NaBH_4 concentration (A) and GO (B) on hydrogen production

Usually, reaction temperature has great impact on the catalysis of chemical reactions. Therefore, the effect of temperature on hydrogen generation catalyzed by $\text{CuFe}_2\text{O}_4/\text{RGO}$ was investigated and the obtained data are presented in Figure 10A. It

was found that the hydrogen production rate gradually increased with increasing of reaction temperature. This is a normal phenomenon for endothermal reaction because high temperature can accelerate the hydrolysis rate of NaBH₄. Though the produced hydrogen volumes by the hydrolysis of NaBH₄ are the same at different temperature, the time needed is different. It was 40, 25, 16 and 13 min respectively as reaction temperature was raised from 30 to 60 °C.

As we know that the activation energy (E_a) shows the temperature dependency of the rate constant for a chemical reaction. It often relies on catalysts, so it is a key parameter to evaluate the performance of a catalyst for NaBH₄ hydrolysis. In order to get the E_a value of NaBH₄ hydrolysis catalyzed by CuFe₂O₄/RGO nanostructures, the rate constants at different temperatures were estimated from the linear parts of the plots in Figure 10A. Then the E_a value was calculated by applying well-known Arrhenius equation (1):

$$\ln k = \ln A - E_a/RT \quad (1)$$

Where, A is a constant known as the Arrhenius factor, k is the rate constant of the reaction at temperature T (in Kelvin), and R is the universal gas constant. Figure 10B illustrates the relationship of lnk versus 1/T. The plot of lnk versus 1/T is linear for the hydrolytic reaction. The slope of the straight line gives an apparent activation energy of 33.95 kJ mol⁻¹. The E_a value of the as-prepared CuFe₂O₄/RGO nanostructures is lower than those of some Cu related catalysts and even noble metal catalysts. Co-Cu-B has an activation energy of 49.6 kJ mol⁻¹ [49], while Cu-Co-supported catalysts provide an activation energy of 42.66 kJ mol⁻¹ [50].

Poly(N-vinyl-2-pyrrolidone)-stabilized Ru-Pd nanoparticles show activation energies of 52.4 and 54.5 kJ mol⁻¹ for the hydrolysis of NaBH₄ and ammonia borane, respectively [51]. This demonstrates that the catalyst prepared in the present work has higher catalytic activity towards hydrogen generation by hydrolysis of NaBH₄.

Figure 10 Effect of temperature on hydrogen production (A); plot of lnk versus 1/T (B)

Recovery of catalysts is important for the re-usage of catalysts and the disposing of waste solution after reaction. It also determines the application cost of a catalyst. Since CuFe₂O₄/RGO nanostructures are magnetic, so they can be easily removed from reaction solution with a magnet. They were rinsed with distilled water for several times before they were reused in the next round of NaBH₄ hydrolysis. The CuFe₂O₄/RGO nanostructures were applied for six successive runs and the catalytic efficiency is shown in Figure 11. The yield of hydrogen is almost 100 %, but the time needed for finishing reaction has been slightly extended. It is similar to the NaBH₄ hydrolysis catalyzed by Pt/C [52] but better than the hydrolysis by Co–Ni–P/Pd–TiO₂ [53]. The results demonstrate that the CuFe₂O₄/RGO nanostructures exhibit good recyclability.

(A)

(B)

Figure 11 Yield of hydrogen (A) and reaction time (B) for six successive catalytic rounds.

Conclusion

A simple hydrothermal method was developed to fabricate CuFe₂O₄/RGO nanostructures. Changing reactant concentration, reaction temperature and reaction time could change the morphology of the CuFe₂O₄ nanoparticles on CuFe₂O₄/RGO. Especially, GO plays an important role in tailoring both the size and shape of the CuFe₂O₄ nanoparticles. The as-prepared CuFe₂O₄/RGO exhibited good catalytic performance toward catalytic hydrolysis of NaBH₄. The hydrogen generation rate reached 622 (mL min⁻¹ g⁻¹) or 1.77 mol H₂ min⁻¹ (mol Cu)⁻¹ for the catalytic

hydrolysis of NaBH_4 , and the activity factor ($33.95 \text{ kJ mol}^{-1}$) was even lower than some noble metal nanoparticles. The high catalytic activity makes $\text{CuFe}_2\text{O}_4/\text{RGO}$ new and cost-effective catalysts for applications in new energies and chemical reactions.

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