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Full Paper

Fabrication of Ti supported NiCo₂O₄ nanosheet array and their superior catalytic performance in the hydrolysis of ammonia borane for hydrogen generation

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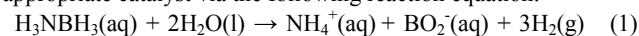
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The development of low-cost nanocatalysts with high activity, high stability and good reusability towards the hydrolysis of chemical hydrides for hydrogen generation is of great importance and significance in the field of hydrogen energy. In this work, Ti supported NiCo₂O₄ thin film of nanosheet array (NiCo₂O₄/Ti) is fabricated by a facile method, and its catalytic performance in the hydrolysis of ammonia borane for hydrogen production is investigated. It is found that the turnover frequency (TOF) of the NiCo₂O₄/Ti can reach 50.1 mol H₂ min⁻¹ (mol catalyst)⁻¹, which is the highest TOF value reported for noble-metal-free catalysts towards the hydrolysis of ammonia borane. The apparent activation energy of ammonia borane hydrolysis in the presence of the NiCo₂O₄/Ti catalyst is as low as ca. 17.5 kJ mol⁻¹. More importantly, the NiCo₂O₄/Ti catalyst can retain ca. 90% of original catalytic activity after 10 cycles, exhibiting much improved durability and the reusability in contrast to many nanocatalysts recently reported in literature. The high catalytic activity, low-cost, together with its good durability and reusability, enable the NiCo₂O₄/Ti to be a strong catalyst candidate towards the hydrolysis of ammonia borane for hydrogen production in the practical applications.

Introduction

The consumption of energy in the world is keeping on rising and the present energy system based on fossil fuels produces a large amount of pollutants, including carbon dioxide, which is regarded as a major cause for "Greenhouse Effect". It is no doubt that seeking for sustainable, environment-friendly and cost-effective energy source is one of the most important tasks in the 21st century. Hydrogen is considered to be an ideal fuel for heating, mechanical power, transportation, as well as electricity generation, on account of the high density of energy (142 MJ/kg), zero emission and sufficient source.^{1,2} Over the past few decades, a number of techniques have been developed to generate and store hydrogen. Particularly, production of hydrogen by catalytic hydrolysis of chemical hydrides, such as NaBH₄, N₂H₄ and NH₃BH₃ (ammonia borane, AB), has received much attention in

view of its high efficiency, convenience and safety.³⁻⁶ For example, three moles of hydrogen will be produced when one mole of AB reacts with two moles of water in the presence of an appropriate catalyst via the following reaction equation:



In the above hydrolytic reaction, the catalyst plays a crucial role in determining the efficiency and rate of hydrogen generation. Over the past decade, it has been well demonstrated that noble-metal-based catalysts, such as Pt,^{5,7} Ru,⁸⁻¹⁰ Pd,¹¹ CoPd,¹² CuPd,¹³ NiPd¹⁴ and PdPt,¹⁵ exhibit relatively high catalytic activity in the AB hydrolysis. However, their large-scale applications were restricted by the high costs and scarcity. In contrast, noble-metal-free catalysts are more attractive due to their greater potential in the practical applications. In recent years, many efforts have been devoted to the development of the low-cost catalysts for the AB hydrolysis and numerous inexpensive nanocatalysts have been reported, including Co,¹⁶⁻¹⁸ Ni,¹⁹ CoB,²⁰ CoP,²¹ Co-Mo-B-P.²² However, most of them suffer from difficult isolation from reaction solution, lower activity in contrast to noble metal catalysts, poor stability or reusability. So, the development of cost-effective, highly active and stable catalysts for AB hydrolysis is highly desirable, which is still a big challenge. On the other hand, most of these low-cost nanocatalysts for AB hydrolysis reported in literature are Co, Ni or their alloys. Therefore, it is of great importance and significance to develop other types of catalysts rather than metals or alloys.

In this work, Ti supported NiCo₂O₄ nanosheet array was fabricated by a facile process and its catalytic performance in the hydrolysis of AB was investigated. It should be mentioned that the NiCo₂O₄ nanostructures for high-performance supercapacitors have been intensively reported over the past several years,²³⁻²⁵ however, their applications as catalysts in heterogeneous catalysis have been seldom concerned. As far as we know, this is the first investigation on NiCo₂O₄ nanostructures as catalysts towards AB hydrolysis for hydrogen production. On the other hand, considering that nanostructured catalysts in the form of film will display better durability and reusability, Ti supported NiCo₂O₄ nanosheet array rather than NiCo₂O₄ nanostructures in the form

of powder is designed in the present study. Considering its low cost, large mechanical strength, together with its high stability in different chemical environment, Ti is selected as the substrate in our work. It is interesting to find that the turnover frequency (TOF) of NiCo₂O₄/Ti in the AB hydrolysis can reach 50.1 mol H₂ min⁻¹ (mol catalyst)⁻¹. To the best of our knowledge, this is the highest TOF value reported in literature for the noble-metal-free catalysts towards AB hydrolysis. In addition, Ti supported NiCo₂O₄ nanosheet array exhibits significantly improved durability and reusability than those nanocatalysts recently reported in literature, which enable it to be a strong catalyst candidate in the AB hydrolysis for the generation of hydrogen in the practical applications.

Experimental Section

Synthesis

All reagents were of analytic grade and used as received without further purification. Double-distilled water was used throughout the experiments. To prepare the NiCo₂O₄ nanosheet array supported on Ti substrate, 4.0 mmol CoCl₂·6H₂O and 2.0 mmol NiCl₂·6H₂O was mixed into 20.0 mL double-distilled water under stirring to form solution A, and 12.0 mmol sodium citrate was dissolved into 20.0 mL water to form solution B. After solution A and B were blended, 40.0 mL NaOH (7.5 M) solution were dropped into the above solution. Afterwards, the mixed solution was quickly transferred into a Teflon-lined steel autoclave, in which a piece of 5 × 12 cm Ti sheet with a thickness of ca. 20 μm and a weight of ca. 0.72 g (purchased from Qingyuan Metallic materials Co., Ltd., China) closely attached to the inner wall of vessel was used as support. Finally, the autoclave was kept in an air oven at 160 °C for 10 h. After that, the sample was transferred into a muffle furnace and subjected to a heat treatment at 400 °C for 4 h. After the reaction, the film was taken out and washed with double-distilled water and acetone, then dried in a vacuum oven at 60 °C for 5 h. For comparison, NiCo₂O₄ nanoparticles were also prepared by a similar process except that no Ti substrate was used in the synthesis. Briefly, CoCl₂·6H₂O, NiCl₂·6H₂O and sodium citrate at molar ratio of 2:1:6 were mixed into water under intense stirring to form a mixed solution. After the addition of NaOH solution, the mixed solution was subjected to a hydrothermal treatment at 160 °C for 10 h. Then, the collected black powder was heated at 400 °C for 4 h.

Characterization

X-ray diffraction (XRD) patterns were recorded using a PANalytical B. V. Empyrean X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406\text{\AA}$). The morphology of the array was investigated using a Hitachi S-4800 field emission scanning electron microscope (FE-SEM). TEM images were obtained on a Tecnai G2 F20 S-TWINT transmission electron microscope. X-ray photoelectron spectra (XPS) was obtained on a VG ESCALAB 210 X-ray photoelectron spectrometer with Al K α radiation. The specific surface area was measured on a Quantachrome Autosorb-1 volumetric analyzer, using nitrogen adsorption and the Brunauer-Emmett-Teller method. The weight of NiCo₂O₄ loaded on the Ti substrate was measured by a Varian 720 Inductively Coupled Plasma-Optical Emission Spectrometer

(ICP-OES).

Catalytic performance testing

The catalytic performance of the NiCo₂O₄/Ti and NiCo₂O₄ nanoparticles were assessed by measuring the accumulative volume of hydrogen generated during AB hydrolysis reaction in a glass reactor connected with a gas burette. Typically, 20.0 mL of freshly-prepared mixed solution of AB (0.15 M) and NaOH (1 M) was added in the reactor. Then, the NiCo₂O₄/Ti (5 cm × 3 cm) was added into the AB solution. The reaction temperature was maintained at 308 ± 0.5 K in a thermostated reactor. The reusability of the NiCo₂O₄/Ti was evaluated by repeating the hydrolysis reaction 10 times in such a model: (1) recollecting the catalyst after reaction; (2) washing the catalyst with water and ethanol alternatively before drying at 50 °C in a vacuum oven; (3) Starting a new run of AB hydrolysis by mixing the catalyst with freshly-prepared AB solution.

Results and discussion

The digital camera photos of bare Ti sheet and NiCo₂O₄/Ti are presented in Fig. S1 (See Electronic supplementary information, ESI). As can be seen, the bare Ti substrate is silver gray with metallic luster (Fig.S1a) while NiCo₂O₄/Ti is black (Fig.S1b), implying the black NiCo₂O₄ has been successfully deposited on the Ti sheet in this study. The microstructures on the surface of Ti substrate and NiCo₂O₄/Ti are investigated by FE-SEM. As can be observed in Fig.1, the Ti substrate is very smooth on its surface (Fig. 1a). In contrast, it became very coarse after the deposition of NiCo₂O₄ (Fig. 1b). Fig.1c reveals that the NiCo₂O₄ layer on the substrate is comprised of NiCo₂O₄ nanosheet array, which looks somewhat like flowers. Fig.1d indicated that the mean thickness of the nanosheets is about 20 nm. Obviously, these nanosheets are not loosely agglomerated but closely interconnected to each other, which are marked with the dotted circles in Fig. 1d. It is worth noting that an ultrasonic treatment of 30 min can not detach these NiCo₂O₄ nanosheets from the Ti substrate, hinting that the as-prepared NiCo₂O₄ nanosheet array is very stable. Besides, a peeling test using scotch tape was also carried out (Experiment details about the peeling test can be seen in ESI), and it was found that no NiCo₂O₄ was detached from the substrate after the test. This further demonstrates the good stability of our sample. Fig. 1e is the TEM image of NiCo₂O₄ nanosheet array, which further confirms the nanostructures of NiCo₂O₄ nanosheets. Fig.1f is the cross-section TEM image of a piece of NiCo₂O₄ nanosheet, demonstrating its thickness of ca. 20 nm. The ICP-OES analysis indicates that the weight of NiCo₂O₄ loaded on Ti sheet (5 × 12 cm) is ca. 9.6 mg.

The crystal structures of the Ti sheet supported NiCo₂O₄, as well as the Ti substrate, were investigated with XRD. As depicted in Fig. 2, seven characteristic peaks at $2\theta = 35.2^\circ$, 38.4° , 40.3° , 53.0° , 63.0° , 70.6° and 76.2° are observed in the XRD pattern of Ti substrate, which can be indexed to the (100), (002), (101), (102), (110), (103) and (112) plane reflections of hexagonal close-packed phase of Ti (PDF#65-9622). Besides these seven peaks, eight characteristic peaks appear in the XRD pattern of NiCo₂O₄/Ti, which can be assigned to the diffractions from (220), (311), (400), (331), (442), (511), (440) and (533) planes of cubic phase of NiCo₂O₄ (PDF#73-1702). This result further confirms that the NiCo₂O₄ has been successfully deposited on Ti substrate.

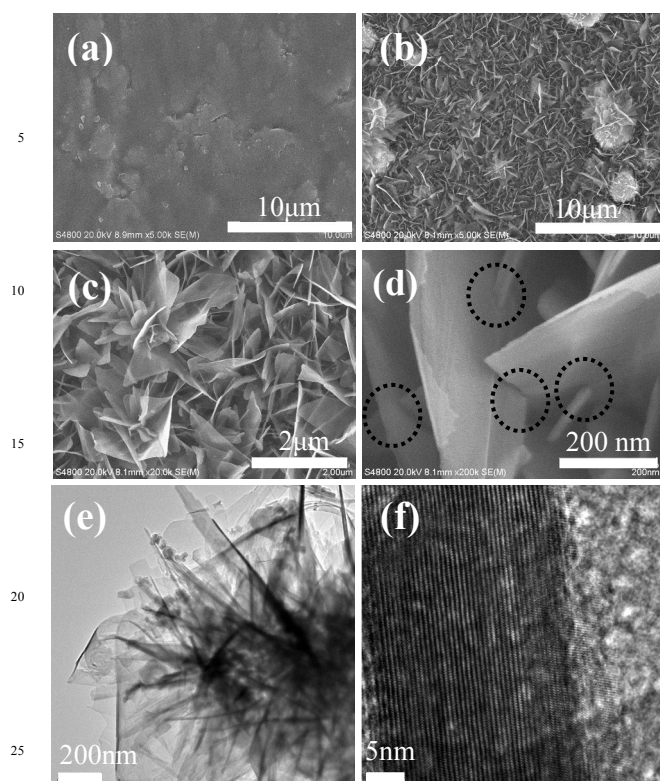


Fig. 1 SEM images of the bare Ti substrate (a) and the NiCo₂O₄/Ti (b, c, d). TEM image of NiCo₂O₄ nanosheet array (e) and cross-section TEM image of a piece of NiCo₂O₄ nanosheet (f).

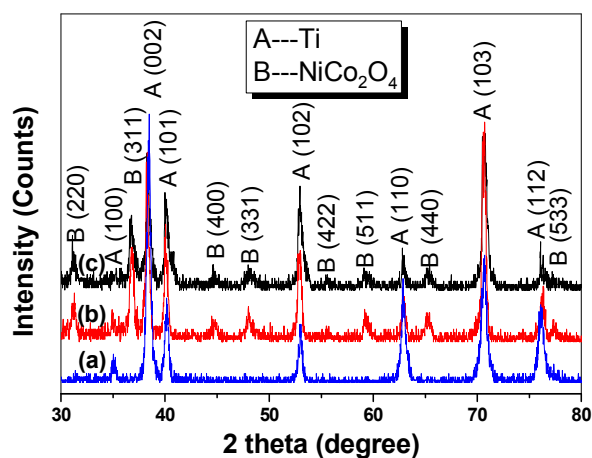


Fig. 2 XRD patterns of the bare Ti substrate (a), the as-prepared NiCo₂O₄/Ti (b) and the NiCo₂O₄/Ti after 10 catalytic cycles (c).

To obtain the information about the chemical states of Co and Ni in NiCo₂O₄/Ti, XPS analysis was carried out. As displayed in Fig. 3, the deconvoluted XPS spectrum shows two peaks at binding energy of ca. 872.8 and 871.3 eV in the region of Ni2p_{1/2}, and two peaks at binding energy of ca. 855.2 and 853.7 eV in the region of Ni2p_{3/2}. The peaks at binding energy of ca. 872.8 and 855.2 eV can be indexed to Ni(III), while those at binding energy of ca. 871.3 and 853.7 can be assigned to Ni(II).²⁶ Similarly, the deconvoluted XPS spectrum shows two peaks at binding energy of ca. 796.0 and 794.7 eV in the region of Co2p_{1/2}, and two peaks

at binding energy of ca. 780.7 and 779.6 eV in the region of Co2p_{3/2}. The peaks at binding energy of ca. 779.6 eV and 794.6 eV can be indexed to Co(III), while those at binding energy of ca. 780.7 eV and 796.0 eV can be assigned to Co(II).²⁶ XPS analysis reveals that Co²⁺, Co³⁺, Ni²⁺ and Ni³⁺ coexist on the surface of NiCo₂O₄/Ti sample, which is similar to the XPS results of the NiCo₂O₄ nanostructures reported by other groups.^{24,26,27}

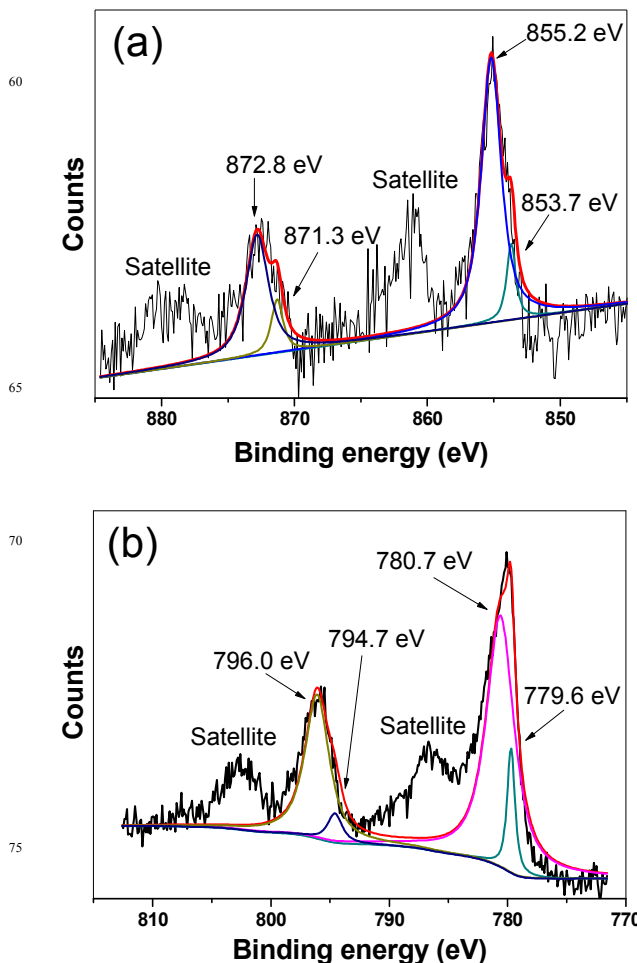


Fig. 3 XPS spectra of NiCo₂O₄/Ti in the regions of Ni 2p (a) and Co 2p (b).

Release of hydrogen from AB solution catalyzed by the as-prepared NiCo₂O₄/Ti was investigated. Firstly, the catalytic activity of Ti substrate in the AB hydrolysis is checked. It was found that nearly no hydrogen is produced from AB solution when the bare Ti sheet is presented in the reaction system, demonstrating that Ti substrate is inactive towards AB hydrolysis. When NiCo₂O₄/Ti is added into AB solution, a certain amount of hydrogen will be generated, suggesting that the NiCo₂O₄ on the Ti substrate can catalyze the AB hydrolysis. Fig. 4a shows the accumulated volume of hydrogen vs. the hydrolysis time at catalyst dosages ranged from 0.3 to 3.6 mg. It is observed that the accumulated hydrogen volume is almost direct proportion to the reaction time at the early stage of the hydrolysis, hinting that the hydrolysis process follows the zero-order kinetics with respect to ammonia borane. To confirm this, a series of catalytic hydrolysis experiments with different initial concentrations of AB were

carried out and the results are shown in Fig.S2 in ESI. As can be seen in Fig.S2, the rate constants almost remain the same despite the fact that the initial concentrations of AB in the catalytic process are different, demonstrating that the hydrolysis process follows the zero-order kinetics with respect to AB. Note that a deviation from linear dependence of the accumulated hydrogen volume with the reaction time was observed at late stage of the hydrolysis reaction, which may result from the external diffusion limitation at low concentration of AB.⁷ The rate constant of AB hydrolysis can be determined from the linear portion of each plot, which can be formulated as the following,

$$k = V / t$$

where k , V , t is the rate constant, accumulated volume of hydrogen and hydrolysis time, respectively. Fig.4b depicts the effect of catalyst dosage on the rate constants. Clearly, k increases linearly with the mass of NiCo_2O_4 . This implies that the hydrogen production rate can be easily controlled by adjusting the amount of NiCo_2O_4 catalysts. It should be mentioned that this is the first investigation on catalytic hydrolysis of AB catalyzed by NiCo_2O_4 and the kinetics data on it is unavailable in literature. For comparison, NiCo_2O_4 particles with a typical diameter of 15-25 nm were prepared and the SEM images are shown in Fig. S3 (See ESI). A series of contrast experiments were carried out, in which the NiCo_2O_4 nanoparticles instead of $\text{NiCo}_2\text{O}_4/\text{Ti}$ acted as catalysts. The rate constants of AB hydrolysis in the presence of the NiCo_2O_4 nanoparticles and the $\text{NiCo}_2\text{O}_4/\text{Ti}$ as catalysts were compared and the results are indicated in Table 1. It is interesting to note that the rate constants of AB hydrolysis for $\text{NiCo}_2\text{O}_4/\text{Ti}$ catalyst are 10-12 times as large as those for NiCo_2O_4 nanoparticles although the BET surface area of $\text{NiCo}_2\text{O}_4/\text{Ti}$ is only ca. 1.4 times as large as that of NiCo_2O_4 nanoparticles. Two factors account for that the $\text{NiCo}_2\text{O}_4/\text{Ti}$ catalyst exhibits better catalytic performance in contrast to the NiCo_2O_4 nanoparticles. Firstly, NiCo_2O_4 layer in $\text{NiCo}_2\text{O}_4/\text{Ti}$ catalysts are composed of nanosheets, which are expected to possess more corners and edges compared with the spherical NiCo_2O_4 nanoparticles. In general, the atoms on the corners or edges have unsaturated valency with less number of bonds around them than those in the interiors or on the faces.^{28, 29} Thus, such atoms will display much higher intrinsic catalytic activity. Secondly, the NiCo_2O_4 nanoparticles suspended in AB solution tend to aggregate on account of the high surface energy. Under such circumstances, the number of active sites of particulate NiCo_2O_4 will drop, which will result in the decrease of their catalytic activity. On the contrary, the NiCo_2O_4 nanosheets in the $\text{NiCo}_2\text{O}_4/\text{Ti}$ catalyst are immobilized on the Ti sheet. In this case, the decline of catalytic performance resulted from the aggregation is avoidable.

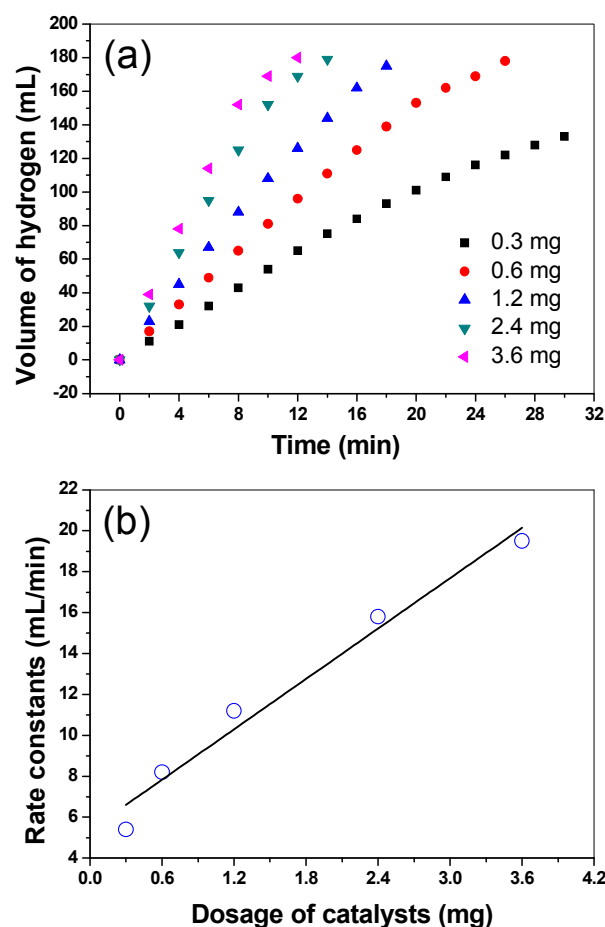


Fig. 4 (a) The accumulated volume of generated hydrogen vs. reaction time at different catalyst dosages; (b) the rate constants at different catalyst dosages.

Table 1 The BET surface of the $\text{NiCo}_2\text{O}_4/\text{Ti}$ and NiCo_2O_4 nanoparticles, and the comparison of rate constants of AB hydrolysis catalyzed by $\text{NiCo}_2\text{O}_4/\text{Ti}$ and NiCo_2O_4 nanoparticles at different dosages.

Sample	Rate constant (min^{-1})					BET surface ($\text{m}^2 \text{g}^{-1}$)
	0.3 mg	0.6 mg	1.2 mg	2.4 mg	3.6 mg	
$\text{NiCo}_2\text{O}_4/\text{Ti}$	5.4	8.2	11.2	15.8	19.5	^a 65.5
NiCo_2O_4 nanoparticles	0.51	0.77	1.03	1.36	1.61	47.2

^a the mass in BET surface of $\text{NiCo}_2\text{O}_4/\text{Ti}$ only counts the mass of NiCo_2O_4 , not including that of Ti substrate.

In this study, AB hydrolysis catalyzed by $\text{NiCo}_2\text{O}_4/\text{Ti}$ catalyst was carried out at different reaction temperatures and the relationship between the volumes of hydrogen with the reaction time is displayed in Fig.5a. It is found that elevating the reaction temperature from 298 K to 308 K will cause a pronounced increase of hydrolysis rate of AB. While a further elevation of temperature to 318 K and 328 K only results in a slight increase of hydrolysis rate of AB. The corresponding TOF value of the $\text{NiCo}_2\text{O}_4/\text{Ti}$ sample at 298 K is figured out to be ca. $50.1 \text{ mol H}_2 \text{ min}^{-1} (\text{mol catalyst})^{-1}$. For comparison, TOF values of some noble-metal-based and noble-metal-free nanocatalysts recently

reported in literature are also listed in Table 2. Evidently, our NiCo₂O₄/Ti catalyst falls into the class of high-performance catalysts towards AB hydrolysis. To the best of our knowledge, among the noble-metal-free heterogeneous catalysts for AB hydrolysis, the NiCo₂O₄/Ti catalyst exhibits the highest catalytic activity in terms of TOF.

The apparent activation energy (E_a) is an important parameter for a catalytic reaction, which can be utilized to assess the overall catalytic activity of a catalyst. Generally, a catalyst with higher catalytic activity always leads to lower activation energy of the catalytic reaction. According to Arrhenius formula, the apparent activation energy of AB hydrolysis catalyzed by the NiCo₂O₄/Ti catalyst can be figured out based on the data on rate constants at different temperatures. Fig. 5b displays the logarithm of rate constants vs. the reciprocal of corresponding reaction temperatures. According to the slope of the fitted line in Fig. 5b, E_a value of AB hydrolysis catalyzed by the NiCo₂O₄/Ti catalyst was calculated to be 17.5 kJ mol⁻¹. This value is even much lower than the E_a value for AB hydrolysis catalyzed by noble-metal-based nanocatalysts (Table 2), hinting the superior catalytic activity of the NiCo₂O₄/Ti catalyst.

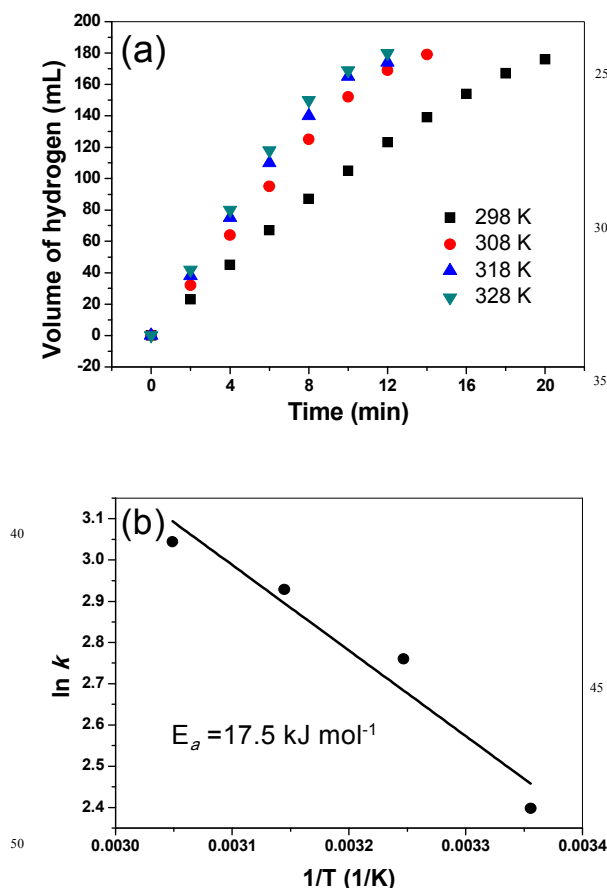


Fig. 5 (a) The accumulated volume of generated hydrogen vs. reaction time at different reaction temperatures; (b) the logarithm of rate constants vs. the reciprocal of reaction temperatures. (Catalyst dosage = 2.4 mg)

Table 2 Comparison of TOF and E_a of different catalysts in AB hydrolysis.

Catalysts	TOF (mol H ₂ min ⁻¹ (mol cat.) ⁻¹)	E_a (kJ mol ⁻¹)	Ref.
Pt cube/CeO ₂ /RGO	48.0	/	30
Pt NPs/CeO ₂ /RGO	30.6	/	30
Ru@Al ₂ O ₃	39.6	48	31
Ru nanoparticles	21.8	27.5	10
Ru/graphene	100	11.7	32
Pd-CDG	15.5	/	33
Pd(0)-HAP	8.3	55	34
RuCu/graphene	135	30.59	35
PtPt nanocubes	50.0	21.8	36
Pt-Pd@PVP	125	51.7	15
Ni ₃₀ Pd ₇₀ /RGO	28.7	45	14
Pd@Co/graphene	37.5	/	37
Co ₃₅ Pd ₆₅ /C	22.7	27.5	12
Ag-Pd/PAN	6.3	/	38
Co/Graphene	13.8	32.75	39
Co-P/TiO ₂	5.3	48.1	40
Electroplated Co-P	10.0	22	21
CoNi/Graphene	16.4	13.49	41
Ni nanoparticles	10.9	/	42
Nanoporous Ni spheres	19.6	27	43
Ni NPs@3D GFs	41.7	/	19
Co film	6.6	59	16
Co-B film	21.6	34	20
NiCo ₂ O ₄	50.1	17.5	This work

The TOF values were either directly taken or calculated from the data given in respective references.

In addition to the activity, the recyclability of a heterogeneous catalyst is of great importance in practical applications. In the present study, hydrolysis of AB catalyzed by the NiCo₂O₄/Ti catalyst was repeated 10 times. The relationship between the accumulated volume of generated hydrogen and reaction time at different cycles is shown in Fig. S4. The normalized rate constant, viz. k_n / k_1 , where k_1 and k_n severally denotes the rate constant of AB hydrolysis in No. 1 and No. n cycle, is utilized to assess the durability and reusability of the NiCo₂O₄/Ti catalyst. As displayed in Fig. 6, the hydrolysis efficiency, it decreases marginally from 96% at the first cycle to 92% at the 10th cycle. As for the rate constant of AB hydrolysis, it almost remains unchanged in the first 6 cycles and decrease slightly in the following cycles. At the 10th cycle, the normalized rate constant is ca. 0.9, indicating that NiCo₂O₄/Ti catalyst still retains 90% of original activity. Our NiCo₂O₄/Ti catalyst exhibit much improved durability and the reusability in contrast to recently reported nanocatalysts, such as Co-graphene (40% activity loss after 5 cycles³⁹), CoNi@graphene (56% activity loss after 5 cycles⁴¹),

Pd-Pt@PVP (39% activity loss after 5 cycles¹⁵), Pt/RGO (54% activity loss after 5 cycles³⁰), Ru/g-C₃N₄ (50% activity loss after 4 cycles⁴⁴), Co film (40% activity loss after 6 cycles¹⁶), intrazeolite Co(0) nanoclusters (31% activity loss after 5 cycles¹⁸).

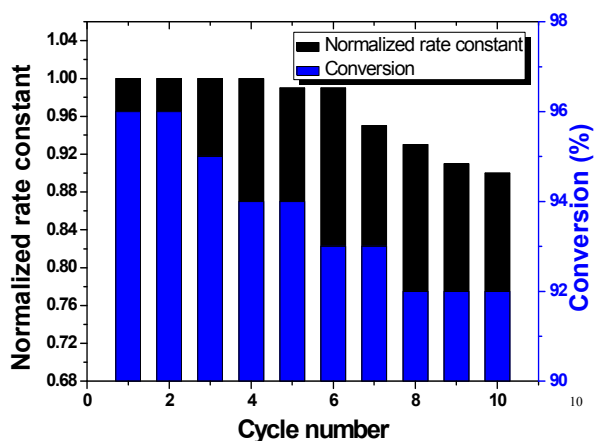


Fig. 6 Normalized rate constants and conversion at different cycles. (Catalyst dosage = 2.4 mg)

For those nanocatalysts in the form of powder, the material loss during the process of separation, drying and re-dispersed will cause the drop of the activity of the catalysts.¹⁸ Also, under the drive of high surface energy, the fine powdery particles are very likely to aggregate during the process of usage, isolation and desiccation, which will result in a remarkable loss of the catalytic activity in the long-term run. In contrast, the NiCo₂O₄ nanosheets in the array are immobilized on the Ti substrate. So, they are exempt from the activity drop caused by the migration and aggregation of the NiCo₂O₄ nanosheets. Besides, the alteration of shapes and morphology of nanocatalysts during catalytic process can also influence their catalytic performance.²⁹ To clarify this, the SEM image of the NiCo₂O₄/Ti after 10 cycles of catalytic reaction are shown in Fig. 7, demonstrating that there were no remarkable morphology changes in the NiCo₂O₄/Ti catalyst. Also, the XRD pattern of the NiCo₂O₄/Ti after 10 cycles is similar to that of the fresh NiCo₂O₄/Ti. These observations hint that our NiCo₂O₄/Ti catalyst is stable and reusable in the reaction of AB hydrolysis.

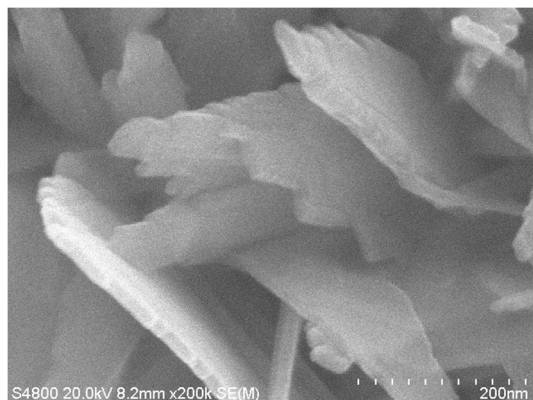


Fig. 7 High-magnification SEM image of NiCo₂O₄/Ti after 10 cycles. (Catalyst dosage = 2.4 mg)

Conclusions

In summary, the array of NiCo₂O₄ nanosheets with a thickness of about 20 nm supported on Ti substrate (NiCo₂O₄/Ti) was successfully prepared. It has been demonstrated that the as-prepared NiCo₂O₄/Ti catalyst exhibits high catalytic performance in the hydrolysis of AB for hydrogen production. The TOF value of the NiCo₂O₄/Ti is 50.1 mol H₂ min⁻¹ (mol catalyst)⁻¹. To the best of our knowledge, this value is higher than those of the other noble-metal-free catalysts in literature. The apparent activation energy of AB hydrolysis in the presence of the NiCo₂O₄/Ti catalyst is as low as ca. 17.5 kJ mol⁻¹. More importantly, the NiCo₂O₄/Ti catalyst still maintain about 90% of original catalytic activity after 10 cycles, exhibiting significantly improved durability and the reusability compared with many other nanocatalysts reported in literature. The high catalytic activity, low-cost, together with its good durability and the reusability enable the NiCo₂O₄/Ti to be a strong catalyst candidate towards the AB hydrolysis for hydrogen generation in the practical applications.

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Notes and references

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Graphic abstract

Ti supported NiCo_2O_4 nanosheet array exhibited high catalytic performance in the hydrolysis of ammonia borane for hydrogen generation.

