



Short communication

Effective hydrolysis of sodium borohydride driven by self-supported cobalt oxide nanorod array for on-demand hydrogen generation

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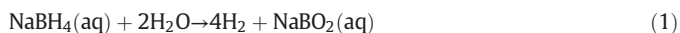
ABSTRACT

Hydrogen storage, distribution and controlled release are of important concerns for hydrogen based economy. Sodium borohydride (NaBH₄) is one of the mostly studied chemical hydrides used for hydrogen storage and generation. However, it requires efficient catalysts to accelerate its dehydrogenation for controllable hydrogen production. In this paper, we demonstrate that the dehydrogenation of NaBH₄ in alkaline solutions can be driven by self-supported cobalt oxide nanorod array on Ti sheet (Co₃O₄ NA/Ti). Such Co₃O₄ NA/Ti shows high catalytic performance with a maximum hydrogen generation rate of 1940 mL/min/g_{Co₃O₄} and an activation energy of 59.84 kJ/mol under ambient condition. Moreover, this catalyst exhibits no mass or activity loss even after 5 cycles with an obvious advantage of easy separation from the fuel solution. This development offers us a cost-effective and recyclable catalytic material toward hydrolytic hydrogen production for applications.

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1. Introduction

Hydrogen has been considered as the cleanest fuel with a key role in our energy landscapes due to its high energy density, zero emission and abundant source [1,2], but its storage, distribution and controlled release are of important concerns for hydrogen based economy [3]. The storage of liquefied hydrogen demands high-energy input and sophisticated equipment and thus is costly. Alternatively, sodium borohydride (NaBH₄) is widely accepted as a promising material to store and deliver hydrogen with several advantages in that it is stable and commercially available with low cost, non-toxicity, non-flammability, high hydrogen content of 10.8 wt% and controlled hydrogen release [4,5]. Hydrolysis of NaBH₄ in the presence of water releases hydrogen forming water-soluble NaBO₂ by product (Eq. (1)):



To suppress the self-hydrolysis of NaBH₄, which is detrimental for on-demand hydrogen generation process, NaOH is often added as a stabilizer. An efficient catalyst however must be used to activate and accelerate the hydrolysis reaction. The most active catalysts are based on noble metals (Pt, Rh, Ru) [5–7], suffering from high cost and limited

supply. Therefore, it is highly attractive to search for low-cost alternatives made of earth-abundant elements.

In recent years, Co-based catalysts, particularly Co_xB alloy, have been widely studied as inexpensive catalysts for NaBH₄ hydrolysis [8–11]. All above studies however utilized Co salts like CoCl₂ and CoSO₄ as catalyst precursors, suffering from poor control over structure and morphology of the catalysts. The availability of rich Co oxides nanomaterials, including 1D nanorods/nanobelts, 2D nanosheets, 3D hollow/hierarchical structures, and hybrid nanostructures, and the well-developed preparative methods promise the use of Co oxides as attractive catalyst precursors [12]. Indeed, recent results demonstrate that LiCoO₂, Co₃O₄ and CoO can be in situ reduced by NaBH₄ to form Co_xB activity phase with improved catalytic activity [13–20]. Moreover, on-demand hydrogen production requires the design of catalyst-supported nanostructure to avoid catalyst aggregation [21] and achieve easy recovery and re-usage. As thus, it is of great need to develop self-supported Co oxide nanostructure as hydrolytic catalyst of alkaline NaBH₄ solution.

In the present study, we report on the use of Co₃O₄ nanorod array supported on Ti sheet (Co₃O₄ NA/Ti) as a non-noble-metal catalyst for the hydrolysis of NaBH₄ in alkaline media with remarkable catalytic activity and durability. It achieves a maximum hydrogen generation rate (HGR) of 1940 mL/min/g_{Co₃O₄} with an activation energy (E_a) of 59.84 kJ/mol under ambient condition. The monolithic nature of this catalyst enables it an on/off switch for on-demand recyclable hydrogen generation.

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2. Experimental section

2.1. Materials

All the chemicals employed were commercially available and used without further purification: $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{CO}(\text{NH}_2)_2$, NH_4F , NaOH and NaBH_4 were purchased from Aladdin Ltd. (Shanghai, China). Ti sheet was rinsed with 1 M HCl at 30 °C for 15 min and then submitted to sonication with acetone, ethanol and deionized water. The water used throughout all experiments was purified through a Millipore system.

2.2. Preparation of Co_3O_4 NA/Ti

$\text{Co}(\text{OH})\text{F}$ precursor was prepared through previously reported method [22]. Typically, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.24 g), NH_4F (0.093 g) and $\text{CO}(\text{NH}_2)_2$ (0.30 g) were dissolved in 25 mL water under vigorous stirring for 20 min. Then the solution was transferred into a Teflon-lined stainless autoclave (40 mL) and a piece of pretreated Ti plate (3 cm \times 2 cm) was immersed into the solution. The autoclave was sealed and maintained at 105 °C for 10 h in an electric oven. After the autoclave cooled down slowly at room temperature, the precursor was taken out and washed with water and ethanol thoroughly before annealing in air at 400 °C for 2 h. Co_3O_4 loading was calculated by measuring the weight difference between bare Ti sheet and Co_3O_4 NA/Ti.

2.3. Characterizations

X-ray diffraction (XRD) characterization was performed on a RigakuD/MAX 2550 diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å). Scanning electron microscopy (SEM) measurements were performed on a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 20 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source.

2.4. Hydrogen generation

Hydrogen evolution from hydrolysis of NaBH_4 was measured using water displacement method. Typically, the hydrolytic dehydrogenation experiments were performed in a 25 mL two-necked round-bottom flask with one neck connected to a gas burette and the other sealed with a rubber cap. The temperature of the reaction system was kept at the desired value by using a constant temperature bath. Co_3O_4 NA/Ti monolithic catalyst was put into alkaline NaBH_4 solution in the two-necked round-bottom flask and the volume of displaced water was automatically calculated using an electronic balance (SHIMADZU, AUW220D, $d = 0.01$ mg) connected to a computer.

3. Results and discussion

3.1. Characterization and hydrogen generation

Co_3O_4 was obtained through a simple thermal decomposition of $\text{Co}(\text{OH})\text{F}$ in air atmosphere. Fig. S1 presents the optical photographs of the bare Ti sheet, the $\text{Co}(\text{OH})\text{F}$ precursor and Co_3O_4 NA/Ti, implying that the black Co_3O_4 has been successfully deposited on the Ti substrate in this study. XRD pattern (Fig. S2a) shows the diffraction peaks at 19.0°, 31.3°, 36.9°, 38.5°, 44.8°, 55.7°, 59.4°, and 65.2° indexed to the (111), (220), (311), (222), (400), (422), (511), and (440) planes of Co_3O_4 , respectively (JCPDS NO. 42-1467) [23–25]. The microstructures on the surface of the Ti substrate and Co_3O_4 NA/Ti are investigated by SEM. As observed in Fig. S2b, HCl treated Ti substrate has a rough surface, which is beneficial to the adhesion of nanorods, and it is fully covered with nanorod array after Co_3O_4 deposition (Fig. S2c and Fig. 1a). It is worth noting that an ultrasonic treatment of 20 min cannot detach these nanorods from the Ti substrate, hinting that the as-prepared Co_3O_4 nanorod array is very stable.

Fig. S2d reveals the optical photographs for the hydrolysis of alkaline NaBH_4 solutions catalyzed by bare Ti sheet and Co_3O_4 NA/Ti, respectively, and it is obviously seen that no hydrogen release occurred for bare Ti sheet, while vigorous bubbles appeared when Co_3O_4 NA/Ti was immersed into alkaline NaBH_4 solution. Thus, Co_3O_4 is the active species

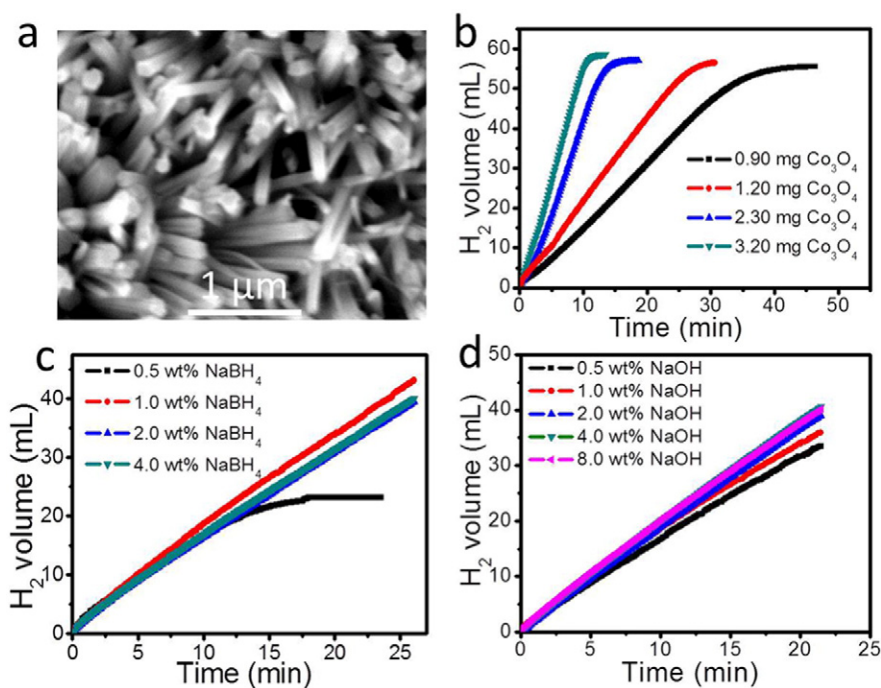


Fig. 1. (a) SEM image for Co_3O_4 NA/Ti. Plots of the volume of hydrogen vs. time from NaBH_4 hydrolysis (3 mL) catalyzed by Co_3O_4 NA/Ti under various conditions: (b) different catalyst amount ($[\text{NaBH}_4] = 1$ wt%, $[\text{NaOH}] = 1$ wt%); (c) different initial NaBH_4 concentrations (Co_3O_4 loading = 0.9 mg, $[\text{NaOH}] = 1$ wt%); (d) different NaOH concentrations (Co_3O_4 loading = 0.9 mg, $[\text{NaBH}_4] = 1$ wt%). All hydrolysis experiments were done at 298 K.

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