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$NiCo_2O_4$ hollow sphere as an efficient catalyst for hydrogen generation by $NaBH_4$ hydrolysis

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ABSTRACT

$NiCo_2O_4$ hollow sphere was successfully synthesized and investigated as a catalyst for the alkali-free hydrolysis of sodium borohydride. Structure and morphologies of nanocomposites were studied by XRD, BET surface area analysis, and SEM-EDX. SEM images of $NiCo_2O_4$ revealed the presence of hollow spherical nanoparticles of average size 3–5 μm. The prepared catalyst displayed high catalytic activity with H_2 generation rate of 1000 mL min^{-1} g^{-1} at room temperature. Furthermore, catalyst could be easily recycled and displayed good stability even after 5 recycles making it suitable for commercial application.

1. Introduction

Development of a low cost and safe method for storage and transportation of hydrogen is important for widespread application of hydrogen as an energy carrier. There are various method reported for hydrogen storage, from which the hydrogen in the form of sodium borohydride ($NaBH_4$) is particularly suitable for portable applications [1]. $NaBH_4$ is a well-known chemical hydride, when $NaBH_4$ react with water, it produces 4 mol of hydrogen per mole of $NaBH_4$ consumed. Since half of this hydrogen is contributed by water, $NaBH_4$ has high gravimetric hydrogen storage capacity of 10.8% [2]. When the catalysts were added to an alkaline $NaBH_4$ solution, the release of hydrogen occurred via the following reaction $NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2\uparrow$ [3,4]. $NaBO_2$ is the non-toxic by-product of $NaBH_4$ hydrolysis, which can be recycled as the starting material for synthesizing $NaBH_4$ [5]. The hydrolysis of $NaBH_4$ is an exothermic reaction but proceeds very gently at room temperature. To accelerate this reaction, it is important to add some acid or a suitable metal catalyst [6]. Nobel metals such as Pt and Ru are the ideal catalyst for this reaction. However, because of its high cost and low abundance, these metals reduces its practicability. Hence it remains challenge to develop low-cost transition metal-based catalytic system for $NaBH_4$ hydrolysis. Co, Ni and their alloys based nanomaterial shows high catalytic activity for hydrogen generation [7]. The monometallic oxide of Ni and Co are very well studied for this reaction, but there are very few reports available of bimetallic oxide of transition metal. Bimetallic $NiCo_2O_4$ of spinel structure is very well known catalyst used in various energy conversion and storage system, catalysis, gas sensor, etc. application. Therefore, the synthesis of spinel oxide $NiCo_2O_4$ has been the target of material chemists. In this field, various morphologies of $NiCo_2O_4$ was prepared using different synthesis routes [8–11]. Among the various $NiCo_2O_4$ nanomaterial, the hollow structured material has a great importance because of their high surface area. But there are only a few reports are available about the fabrication of $NiCo_2O_4$ hollow spheres, especially using soft-chemical methods. Herein we report the synthesis of $NiCo_2O_4$ hollow spheres by hydrothermal followed by air annealing route, and successfully used as a catalyst for $NaBH_4$ hydrolysis.

2. Experimental

In a typical synthesis glucose (30.0 mmol) was dissolved in 120 mL of distilled water then Nickel (II) chloride hexahydrate (2.0 mmol), Cobalt (II) chloride hexahydrate (4.0 mmol) and urea (50.0 mmol) above solution stirred 45 min and then placed in 200 mL capacity Teflon-lined stainless steel autoclave, which was heated in an oven to 180 °C for 24 h. The product was filtered off and washed several time, first with distilled water and then ethanol, and finally dried in a vacuum oven at 70 °C for 6 h. After synthesis, the metal hydroxide- carbon composites were annealed at 400 °C (heating rate of 3 °C/min) for 4 h to remove the carbon core, leading to the formation of hollow $NiCo_2O_4$ sphere.

A previously reported water displacement method (Fig. 1(a)) was used to determine the amount of the hydrogen generated

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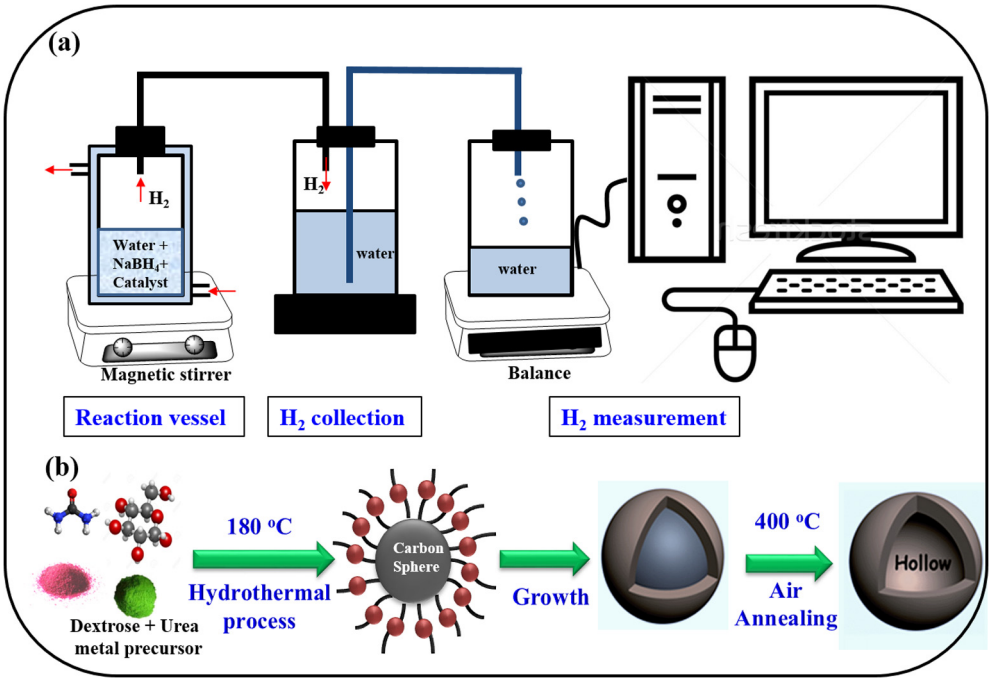

Fig. 1. (a) Water displacement method, (b) Formation mechanism of $NiCo_2O_4$ Hollow sphere.

[12]. In a typical experiment, an aqueous solution containing 1 wt% $NaBH_4$ and 0.04 wt% catalyst in 50 mL distilled water was placed inside the glass reactor kept in an isothermal bath. This reactor was connected to a sealed flask filled with water. Water displaced from this flask due to hydrogen generated in the reaction was collected in a collector flask placed on an electrical balance. Change in weight of the collector flask was recorded as a function of time using a computer program and directly correlated to the volume of hydrogen generated.

3. Results and discussion

Fig. 1(b) shows the formation mechanism of $NiCo_2O_4$ hollow sphere. During hydrothermal treatment at 180 °C, the dextrose initially loses water (T = 160 °C) through an intermolecular condensation reaction and subsequently an aromatization process occurs [13], leading to formation of carbon sphere. Simultaneously Under hydrothermal reaction condition at 180 °C, Urea decomposes slowly with releasing CO_2 and NH_3 followed by their hydrolysis producing CO_3^{2-} and OH^- ions [14]. Because of basic NH_3 the solution becomes alkaline, that helps to promote nucleation of Co and Ni species. That nucleation takes place on the surface of carbon sphere. Here, the carbon sphere act as template. When we annealed this sample at 400 °C in air atmosphere, the decomposition of carbon takes place that create a cavity inside a ball. Along with this transformation the $NiCo_2(OH)_6$ oxidation take place simultaneously, leading to formation of $NiCo_2O_4$ hollow sphere.

The crystal structure and phase purity of $NiCo_2O_4$ hollow sphere was identified using XRD pattern as shown in Fig. 2(a). The XRD pattern match well with cubic $NiCo_2O_4$ (JCPDS No. 01-073-1702) with the space group of *Fd*3*m* (227). No other impurities were detected in the XRD patterns which confirm the complete decomposition of as prepared precursor into $NiCo_2O_4$. The average crystallite size of the prepared $NiCo_2O_4$ hollow sphere calculated according to Scherrer's formula is around 93.17 nm. The porosity of material confirmed by N_2 adsorption-desorption isotherm curve and we found that the BET specific surface area of $NiCo_2O_4$ hollow sphere is around 42 $m^2\ g^{-1}$. Fig. 2(b) clearly indicate that the samples presented type III isotherm with characteristic H3 hysteresis disc indicating the existence of highly porous structure. In inset Fig. 2(b), we can clearly see that the peak at 8.3 nm is most dominant, which concludes that the material is mostly mesoporous. The morphology of the prepared $NiCo_2O_4$ was characterized using FE-SEM. Fig. 2(c) and (d) shows the FE-SEM image of samples before calcination, from that we can clearly see that before calcination the morphology of material is rigid ball like with an average size of 4–6 μm. after calcination in air atmosphere at 400 °C the inside carbon core removes and $NiCo_2(OH)_6$ rigid sphere is converted to $NiCo_2O_4$ hollow sphere. In addition, we also applied energy dispersive X-ray spectroscopy (EDX) and element mapping analysis to understand the elemental composition as well as element distribution on the surface of $NiCo_2O_4$-hollow sphere. The EDX analysis showed in Fig. 3(h), which confirm the presence of Ni, Co, C and O element in hollow sphere. Fig. 3(g) also shows the elemental mapping of single $NiCo_2O_4$-hollow sphere. From which we can clearly see that the distribution of Co, Ni, O and C element on the surface of hollow sphere is uniform.

Among the various metal borohydrides, $NaBH_4$ was chosen as H_2 generating material in our experiments mainly because of its relatively moderate rate of hydrolysis compared to other metal borohydrides and its higher solubility (56 g per 100 g H_2O). We screened different catalyst for $NaBH_4$ hydrolysis at 25 °C (Fig. 3 (a)). As we are using in situ formed carbon sphere as a template, we tested carbon sphere, which was prepared using previously reported procedure. We found that the hydrolysis rate for carbon sphere is very slow (Fig. 3(a) blue curve). The as prepared $NiCo_2(OH)_6$ rigid sphere also shows very less activity. But when we tested $NiCo_2O_4$ hollow sphere catalyst for H_2 generation. We found that it shows higher activity for $NaBH_4$ hydrolysis with the H_2 generation rate of 1000 mL $min^{-1}\ g^{-1}$. In metal catalysis system temperature is a suitable experimental parameter to study maximizing activity in chemical processes [15]. Activity test of $NiCo_2O_4$ hollow sphere catalyst was carried out at different temperatures (i.e., 10, 20, 30 and 40 °C) at constant time 25 min in isothermal reactor bath. We found that with increasing temperature the reaction time became smaller (Fig. 3(b)). The hydrogen production became more