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Cobalt oxide synthesized using urea precipitation method as catalyst for the hydrolysis of sodium borohydride

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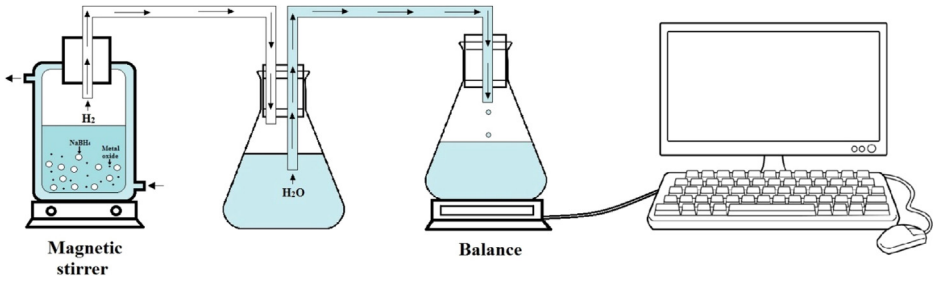
HIGHLIGHTS

- A simple and cost effective method for Co_3O_4 nanorods synthesis is reported.
- Urea is an attractive material as precipitation agent for preparing Co_3O_4 nanorods.
- Co_3O_4 shows excellent catalytic activity for hydrogen production.
- Co_3O_4 nanorods can be recycled and reused without any apparent loss of activity.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we report a simple precipitation method for cobalt oxide (Co_3O_4) nanorods synthesis using cobalt chloride and urea in aqueous solution. The obtained samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) analysis, transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR). The characterization results indicate that urea is an attractive material that can be used as precipitation agent for preparing Co_3O_4 nanorods by controlling synthesis condition. The catalytic activity of as-prepared material was investigated for hydrolysis reaction of sodium borohydride and it is found that Co_3O_4 nanorods shows excellent hydrogen production in title reaction. After reaction course, Co_3O_4 nanorods can be recycled and reused without any apparent loss of activity which makes this process cost effective and hence ecofriendly.

1. Introduction

Production of hydrogen gas from sodium borohydride ($NaBH_4$) has gained much attention for the past few years. This is mainly because $NaBH_4$ is the least expensive metal hydride available commercially. It also contains high theoretical hydrogen content of 10.8 wt% and its solution has an excellent stability under high pH value at ambient temperature [1,2]. In addition, high quality hydrogen can be produced controllably from the hydrolysis of $NaBH_4$ in the presence of certain catalysts [3]. Synthesizing an efficient catalyst plays a great role in the process of hydrogen generation from hydrolysis of $NaBH_4$.

Many catalysts have been developed for the hydrolysis of $NaBH_4$ including but not limited to acids and metals. The use of acid as a homogenous catalyst for $NaBH_4$ hydrolysis has been reported as early as 1953 [4]. The major advantage of using acid catalysts includes production of a very dry hydrogen gas, easy control of hydrogen production and environmentally safe waste products formed during the reaction. However, this is compensated by the disadvantage of carrying a strong acid reservoir which complicates

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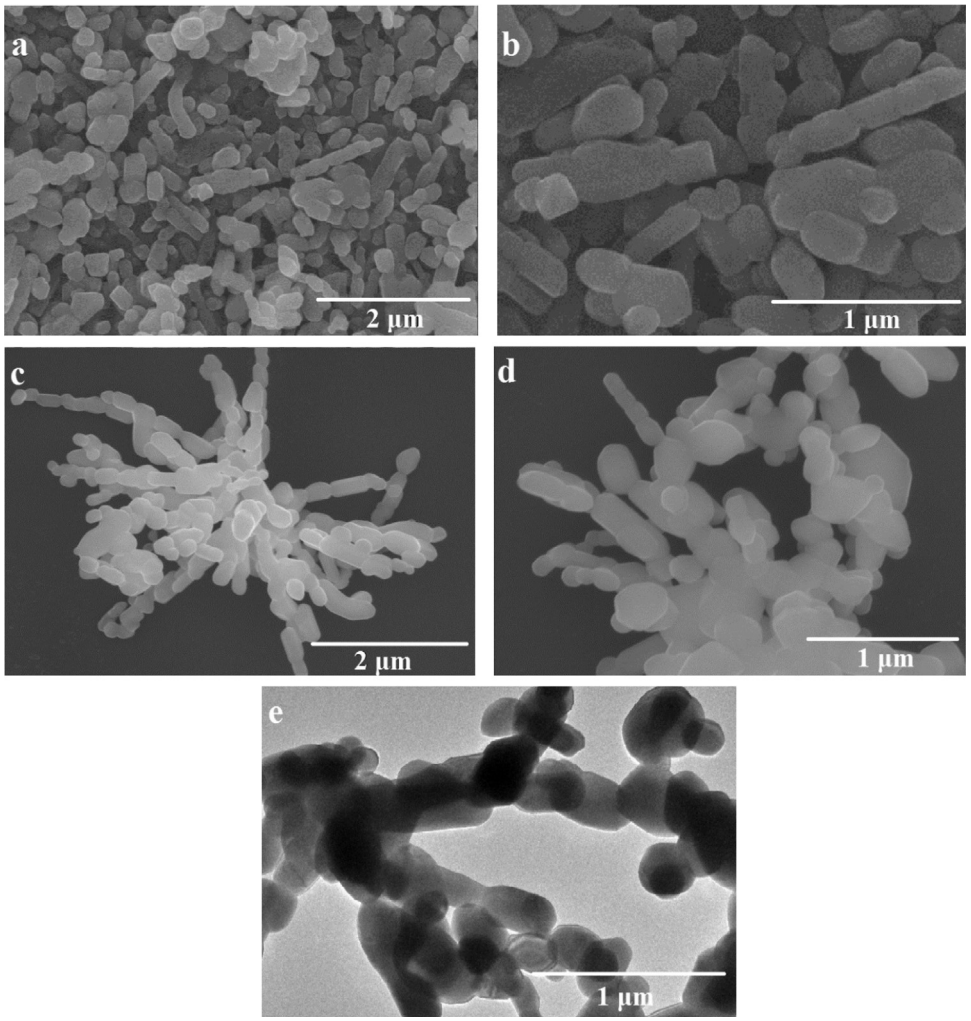

Fig. 1. Low and high magnification SEM images of the synthesized Co_3O_4 nanorods during 8 h reaction time (a–b) and 12 h reaction time(c–d); TEM image of the synthesized Co_3O_4 nanorods during 12 h reaction time.

the reactor design [5]. Additionally, several studies showed that noble metals such as Pt [6], Rh [7], Ru [8,9], etc. exhibit good catalytic effect on $NaBH_4$ hydrolysis but high cost and relatively less abundance have hindered the application of noble metals.

Because of the drawbacks of noble metals, the interest on developing a cheaper but efficient alternative catalyst for the hydrolysis of $NaBH_4$ has been growing. With this, increasing attention has been given to cobalt and cobalt based catalyst precursors such as cobalt salts, cobalt borides, and cobalt based alloys [10,11]. Cobalt based materials become reduced in-situ by $NaBH_4$ to form the active catalyst, identified in many cases to be Co $_x$B, prompting them to be called catalyst precursors in hydrolysis systems [12–15]. Despite the many attractive features of Co as an alternative to precious metal catalyst, drawbacks include lengthy and involved synthesis methods and the pyrophoric nature of elemental nano-sized cobalt in air to rapidly form Co_3O_4. Moreover, studies regarding the use of Co_3O_4 as a catalyst precursor for hydrolysis of $NaBH_4$ solutions and $NaBH_4$/NaOH solutions yielded promising results [16–21]. However, a very little effort has been taken to improve the stability, morphology and catalytic activity of pure Co_3O_4.

The motivation for this study is to evaluate the efficiency of Co_3O_4 prepared via urea precipitation method as catalyst in $NaBH_4$ hydrolysis. Specifically, this work presents a modified urea precipitation methodology that produces a uniform, high purity, high surface area nanorods Co_3O_4, along with subsequent hydrogen generation rate (HGR) performance as a catalyst precursor for $NaBH_4$ hydrolysis. In this work, the morphology of as synthesized Co_3O_4 powders is evaluated by SEM, TEM, BET, FTIR and XRD. HGR is assessed by traditional water displacement method and are related to performance to assess the impact of crystallinity and morphology on conversion efficiency from catalyst precursor to active catalyst in the hydrolysis of $NaBH_4$.

2. Experimental

2.1. Chemicals

Cobalt (II) chloride hexahydrate ($CoCl_2{\cdot}6H_2O$), urea (N_2H_4CO), $NaBH_4$ was purchased from Sigma Adrich, USA and used as received.

2.2. Preparation of Co_3O_4 nanorods

The Co_3O_4 nanorods were prepared by modified urea precipitation method. In typical experiment, cobalt salt ($CoCl_2.6H_2O$) and urea (in a 1:5 molar ratio) were charged in a 100 mL sealed borosil glass bottle containing sufficient water, keeping the concentration of the metal salt in 0.1 M. The mixture was homogenized by ultrafine sonication and then heated to 100 °C where it was held for