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# Chitosan-mediated Co–Ce–B nanoparticles for catalyzing the hydrolysis of sodium borohydride

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## ARTICLE INFO

### Article history:

Received 20 October 2017

Received in revised form

23 November 2017

Accepted 19 January 2018

Available online xxx

### Keywords:

Co–Ce–B

Chitosan-derived carbon

Catalytic activity

NaBH<sub>4</sub>

Hydrolysis

## ABSTRACT

Highly dispersed Co–Ce–B nanoparticles supported on chitosan-derived carbon (Co–Ce–B/Chi–C) were synthesized through chemical reduction and carbonization. The morphology and microstructure of the Co–Ce–B/Chi–C nanocomposite were characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and Brunauer–Emmett–Teller adsorption analysis. This nanocomposite had uniform morphology and large surface area, and it showed high catalytic activity for NaBH<sub>4</sub> hydrolysis and good cycle stability. Compared with unsupported Co–Ce–B particles, this nanocomposite showed greatly increased catalytic activity for NaBH<sub>4</sub> hydrolysis. A remarkably high hydrogen generation rate of 4760 mL<sup>−1</sup> min<sup>−1</sup> g<sup>−1</sup> at 30 °C was achieved with low activation energy of 33.1 kJ mol<sup>−1</sup>. These results indicate that the Co–Ce–B/Chi–C nanocomposite is a promising catalyst for on-demand hydrogen generation via NaBH<sub>4</sub> hydrolysis.

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## Introduction

Hydrogen for use in fuel cells can be produced efficiently and inexpensively from boron-hydrides [1–3]. Generally, boron-hydrides are decomposed by thermolysis or hydrolysis to produce hydrogen [4]. Thermolysis is usually performed at high temperature, and it inevitably produces toxic species that are harmful to fuel cells [5,6]. Therefore, studies have tried to improve the feasibility of the thermolysis of boron-hydrides [7]. However, thus far, no practical boron-hydrides that release hydrogen at the operating temperature of hydrogen fuel cells have been found [4]. Alternatively, hydrolysis can be used to produce hydrogen from boron-hydrides easily and in a controllable way under friendly conditions [8–12]. The byproduct of this reaction is nontoxic and

can be recycled for regeneration [12–14]. However, this reaction is sluggish at room temperature. Therefore, active catalysts are required to accelerate the hydrolysis reaction. As a result, various catalysts have been studied for the hydrolysis of boron-hydrides [8,9,15–22].

Because the catalytic hydrolysis of boron-hydrides is a heterogeneous reaction [10], catalysts with high surface area and good dispersion are preferred. Doping the active components or supporting them on a porous substrate is a feasible way to increase the surface area of catalysts [20,23–26]. For instance, Tang et al. doped a Co–P nanoarray with Fe to obtain a monolithic multifunctional catalyst that showed high activity for NaBH<sub>4</sub> hydrolysis under alkaline conditions [27]. Mori et al. carbonized an Ru complex to obtain a highly dispersed Ru/C catalyst that showed high activity for ammonia borane

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<https://doi.org/10.1016/j.ijhydene.2018.01.125>

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hydrolysis [28]. These reports provided a useful guide for designing high-performance catalysts for the hydrolysis of boron-hydrides. However, it remains challenging to obtain active catalysts through a simple process using inexpensive starting materials.

Co–B alloy has been studied widely as a catalyst for the hydrolysis of boron-hydride owing to its excellent catalytic properties, easy preparation, and low cost [1,9,29]. However, its nanoparticles can aggregate easily in an aqueous solution because of their high surface energy and the exothermic synthesis process. Transition or rare earth metals can be introduced in the alloy to increase the nanoparticle dispersion [10,20,30–34]. In particular, rare earth metals not only enhance the catalytic activity but also increase the corrosion resistance of the catalyst [30,35–37]. In the present study, Cerium (Ce) was introduced in Co–B alloy, and the synthesis of Co–Ce–B nanoparticles was mediated using chitosan. The metal salts were dissolved in the chitosan hydrogel and reduced using NaBH<sub>4</sub>. Chitosan acted as a stabilizer to inhibit the aggregation of Co–Ce–B nanoparticles. Moreover, chitosan is a precursor to produce a carbon support. Ultimately, highly dispersed Co–Ce–B nanoparticles on chitosan-derived carbon (Co–Ce–B/Chi–C) were obtained. The as-prepared Co–Ce–B/Chi–C nanocomposite showed high catalytic activity for NaBH<sub>4</sub> hydrolysis at room temperature as well as good cycling stability.

## Materials and methods

### Synthesis of Co–Ce–B/Chi–C nanocomposite

All chemicals were obtained from commercial sources and used without further purification. Deionized water was used to prepare all solutions. To prepare Co–Ce–B/Chi–C, 0.5 g of chitosan was first dissolved in 50 mL of 1 wt% acetic acid solution under stirring. The pH of the chitosan hydrogel was adjusted to 4 by gradually adding concentrated NaOH solution. Next, CoSO<sub>4</sub>·7H<sub>2</sub>O (4.22 g, 15 mmol) and Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (1.3 g, 3 mmol) were dissolved in this hydrogel, and the resulting solution was stirred for 1 h. Then, 10 mL of 20 wt% NaBH<sub>4</sub> was added dropwise to this solution, and it was stirred for 4 h. The solution was then dried in a vacuum oven at 60 °C for 24 h. The resulting solid was ground into a fine powder. This powder was then placed in a tube furnace and heated to 400 °C at a heating rate of 5 °C/min under nitrogen (N<sub>2</sub>) atmosphere, and the temperature was kept constant for 3 h. Then, the powder was allowed to cool down to room

temperature under N<sub>2</sub> atmosphere. Finally, the resulting black Co–Ce–B/Chi–C powder was washed with a 2 M HCl solution and water thoroughly and dried in a vacuum oven at 60 °C for 5 h. Fig. 1 shows the scheme of its preparation process. For comparison, Co–Ce–B and Co–Ce–B/Chi (not carbonized) were prepared under identical conditions. Hereafter, Co–Ce–B/Chi–C refers to the sample prepared as described above unless mentioned otherwise.

### Catalyst characterization

Scanning electron microscopy (SEM; Quanta 200) and transmission electron microscopy (TEM; JEOL 2010) were used to characterize the morphology and microstructure of the catalyst powder. An Oxford energy dispersive X-ray spectrometer (EDX) attached to the SEM was used to analyze the elemental composition of the particles. Thermogravimetric analysis was conducted using a thermal analyzer (TG Q600) at a heating rate of 5 °C min<sup>-1</sup> in N<sub>2</sub> flow (15 mL/min). The composition of the catalyst samples was analyzed using inductively coupled plasma atomic emission spectrometry (ICP-AES, Optima 8000, PerkinElmer, USA). X-ray photoelectron spectroscopy (XPS; ESCA 250) was used to investigate the surface electronic states of the samples with the aid of an Al K<sub>α</sub> excitation source. The crystal structure of the samples was determined using an X-ray diffractometer (XRD; D8 Advance, Bruker) with Cu K<sub>α</sub> radiation ( $\lambda = 1.5418 \text{ \AA}$ ). N<sub>2</sub> adsorption–desorption isotherms were recorded using a Quantachrome Autosorb-iQ2 Automated Gas Sorption System at 77 K. The specific surface areas and pore-size distributions of the samples were calculated using the Brunauer–Emmett–Teller and density functional theory methods, respectively.

### Hydrogen generation measurement

The volume of hydrogen generated was measured using a lab-made system by the water displacement method. Details about the same are presented in our previous paper [38]. Briefly, a solution containing 1.5 wt% NaBH<sub>4</sub> and 5 wt% NaOH was placed in a thermostatic water bath until it reached equilibrium. Then, 10 mL of this solution was injected into a flask containing 0.15 g of the catalyst. To measure the reaction kinetics, the flask was heated to different temperatures. The stability of the catalyst was monitored by the variation of the hydrogen generation (HG) rate. After the hydrolysis reaction was completed, the catalyst was centrifuged and washed with water several times. The recycled catalyst was then added to a new batch of NaBH<sub>4</sub> solution (10 mL).

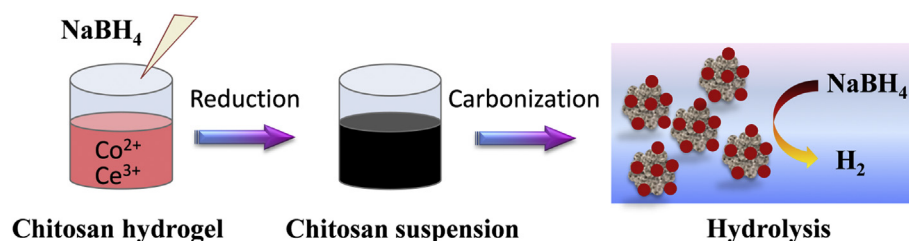


Fig. 1 – Scheme of preparation process of Co–Ce–B/Chi–C.

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