



Short Communication

Graphene supported Ru@Co core–shell nanoparticles as efficient catalysts for hydrogen generation from hydrolysis of ammonia borane and methylamine borane



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ARTICLE INFO

Article history:

Received 19 July 2013

Received in revised form 29 August 2013

Accepted 2 September 2013

Available online 12 September 2013

Keywords:

Core–shell

Ruthenium

Cobalt

Graphene

Hydrogen storage

ABSTRACT

Well-dispersed graphene supported Ru@Co core–shell nanoparticles were synthesized by one-step in situ co-reduction of aqueous solution of ruthenium(III) chloride hydrate, cobalt(II) chloride hexahydrate and graphite oxide (GO) with ammonia borane under ambient condition. The as-synthesized nanoparticles exert excellent catalytic activities, with the turnover frequency (TOF) value of $344 \text{ mol H}_2 \text{ min}^{-1} (\text{mol Ru})^{-1}$ for catalytic hydrolysis of ammonia borane, which is the second highest value ever reported. The as-synthesized catalysts exert superior catalytic activities than the monometallic (Ru/graphene), alloy (RuCo/graphene), and graphene-free Ru@Co counterparts towards the hydrolytic dehydrogenation of AB. Moreover, the catalytic hydrolysis of MeAB at room temperature was also studied. These Ru@Co NPs are a promising catalyst for amine-borane hydrolysis and for developing a highly efficient hydrogen storage system for fuel cell applications.

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1. Introduction

Safe and efficient storage of hydrogen is essential for the development of a hydrogen-based energy infrastructure [1]. Recently, numerous hydrogen storage approaches are currently under investigation, including metal hydrides [2], sorbent materials [3], and chemical hydride systems [4]. Among the chemical hydrides, ammonia borane ($\text{NH}_3\text{-BH}_3$, AB) has recently received a great interest because of its 19.6 wt.% hydrogen content, and its being highly stable and environmentally benign [5]. Hydrolytic dehydrogenation of AB is considered to be the most convenient approach for portable hydrogen storage application [6]. However, the methyl-substituted AB, methylamine borane ($\text{CH}_3\text{NH}_2\text{-BH}_3$, MeAB) with the 11.1 wt.% hydrogen content, has not been widely studied [7]. Furthermore, to the best of our knowledge, the hydrolysis of MeAB, which could also release 3 mol H_2 per mol MeAB at room temperature has been rarely reported. Therefore, searching for suitable catalysts that meet efficient, economical, and stable requirements toward hydrogen generation from the amine–borane systems under moderate conditions, is crucial for their practical applications.

On the other hand, bimetallic transition metal core–shell nanoparticles (NPs) have attracted considerable interest owing to their unique optical properties [8], electronic properties [9], and exciting potential for application in biological [10], chemical sensing [11], optoelectronics [12], magnetism [13], and catalysis [14]. Such materials are often

found to possess enhanced catalytic properties in contrast to the monometallic counterparts and alloys, due to the interplay of electronic and lattice effects of the neighboring metals [15]. Ru nanoparticles, including monometallic Ru-based NPs [16] and bimetallic RuCo [17], RuNi [18], and Ni@Ru [19] NPs, have showed extremely high activities for catalytic dehydrogenation of AB. Recently, the synthesis of Ru@Ni core–shell NPs has been reported by a spray-pyrolysis method [20], however, as far as we know, there are no reports about synthesis and characterization of Ru@Co core–shell NPs. Therefore, developing a facile one-step route to construct the Ru-based core–shell NPs with high catalytic activities are highly desirable.

Herein, we first report the in situ synthesis of magnetically recyclable graphene supported Ru@Co core–shell NPs using AB as reductant in a one-step co-reduction route at room temperature under ambient atmosphere. Graphene was chosen as a support because it has been reported to be a suitable substrate to grow active materials and maintain the stability of the metal NPs during the catalytic process [21], due to its outstanding charge carrier mobility [22], thermal and chemical stability [23], and high specific surface area [24], etc. The as-synthesized catalysts exert superior catalytic activities than the monometallic (Ru/graphene), alloy (RuCo/graphene), and graphene-free Ru@Co counterparts towards the hydrolytic dehydrogenation of AB. Moreover, the catalytic hydrolysis of MeAB at room temperature was also studied.

2. Experimental

The detailed experimental process could be found in the Supporting information.

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3. Results and discussion

3.1. Synthesis and characterization

The graphene supported core-shell Ru@Co/graphene NPs were prepared by adding AB into the precursor solution containing

RuCl₃, CoCl₂, and graphene oxide (GO) at room temperature. The Ru³⁺ and Co²⁺ were reduced in sequence to produce core-shell structured NPs during the reduction process. Considering the reduction potentials of Ru³⁺ and Co²⁺ ($E^0(\text{Ru}^{3+}/\text{Ru}) = +0.40 \text{ eV vs. SHE}$; $E^0(\text{Co}^{2+}/\text{Co}) = -0.28 \text{ eV vs. SHE}$), Ru³⁺ with higher reduction potential was first reduced by AB, and

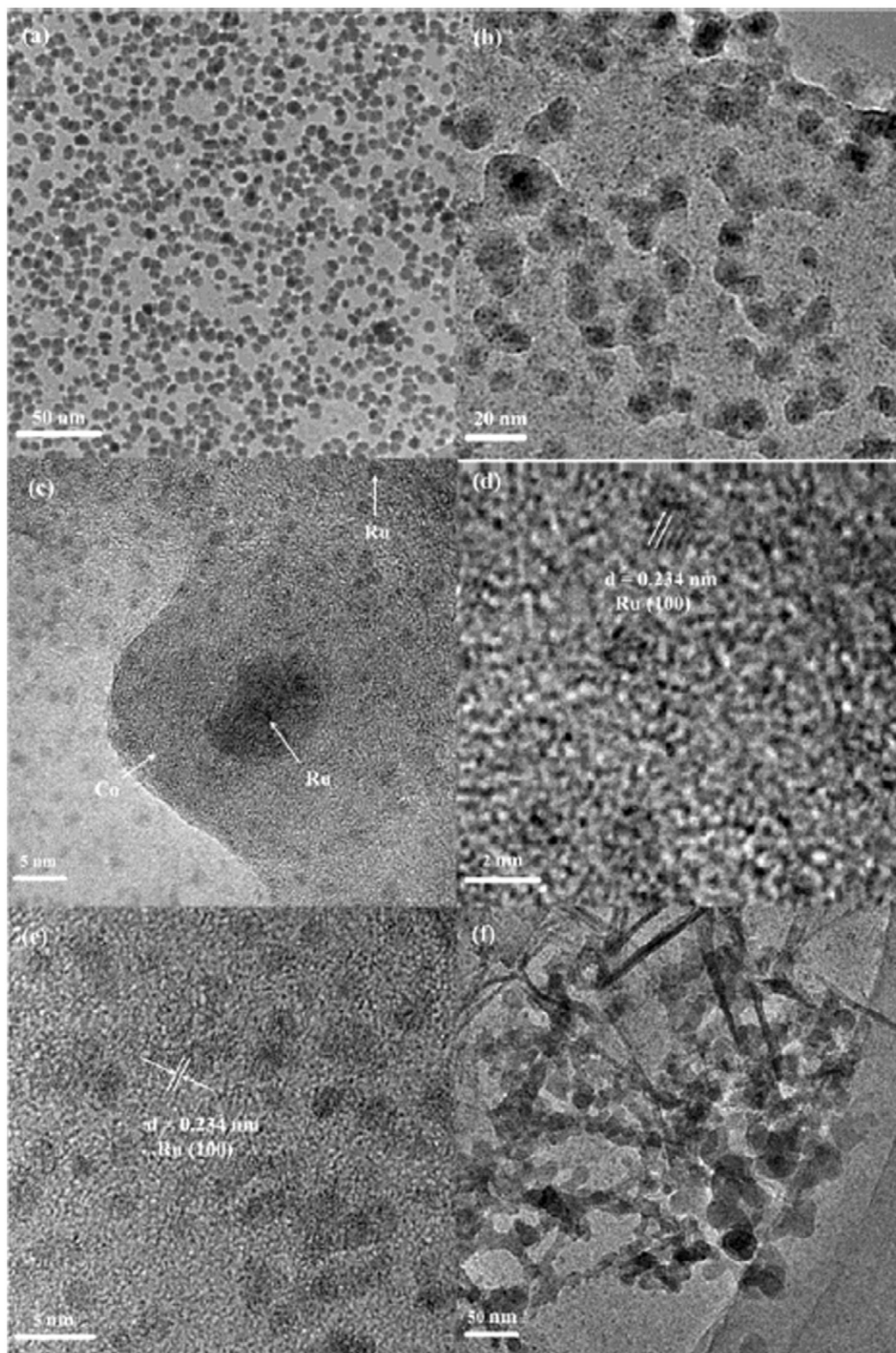


Fig. 1. (a)–(d) TEM images of the composite of Ru and Ru@Co/graphene NPs with different magnifications; (e)–(f) TEM images of the as-synthesized NPs after the fifth cycle.

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