Facile synthesis of monodisperse ruthenium nanoparticles supported on graphene for hydrogen generation from hydrolysis of ammonia borane

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ABSTRACT

Monodisperse ruthenium (Ru) nanoparticles (NPs) supported on graphene have been synthesized by co-reduction of $RuCl_3$ and graphite oxide in ethylene glycol using ascorbic acid as reducing agents. Thanks to the narrow size distribution of Ru NPs and the synergistic effect with graphene, the as-synthesized Ru/graphene exerts exceedingly high catalytic activity toward hydrogen generation from hydrolysis of ammonia borane, with the turnover frequency (TOF) value of 600 mol H_2 min^{-1} (mol Ru)$^{-1}$, which is among the highest value ever reported.

Introduction

Metallic nanoparticals (NPs) with narrow size distribution have attracted considerable interest owing to their highly catalytic performances [1–5]. However, small metallic NPs with high surface energy have the inherent tendency to agglomerate, which leads to a vital decrease in their catalytic performances [6,7]. To solve this problem, numerous bottom-up synthetic approaches have been explored with the aim of generating metal NPs with controlled size and protecting them from agglomerating into the bulk metal. Graphene, a two dimensional one-atom-thick layer of sp^2 hybridized carbon atoms has been considered as one of the most appealing carbon support because of its high electronic transport, strong mechanical properties, thermal and chemical stability, and excellent physical and chemical properties [8–10]. Loading metal NPs onto graphene is expected to coat the surface of NPs, prohibit the aggregation. Furthermore, the catalytic performances could be enhanced due to the charge transfer across the graphene-metal interface [11]. To this end, the graphene-supported nanohybrids have received considerable attention owing to their potential applications in catalysis, optoelectronics, sensors, and energy conversion [12,13].

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On the other hand, the search for safe and efficient hydrogen storage material is still the key issue for the development of hydrogen economy. Among the various chemical hydrogen storage materials, ammonia borane (NH_3-BH_3, AB) has been considered as one of the most compelling candidates due to its high gravimetric hydrogen density (19.6 wt% hydrogen content), high stability, environmental benignity, and favorable kinetics of hydrogen release [14]. To date, a number of noble and non-noble metal based nanocatalysts have exhibit high efficacy for hydrogen generation from hydrolysis of AB [15–18]. The metal NPs prepared in the presence of surfactants and stabilizing polymers allows the fine control over the size and shape of the metal NPs, however, the purification requires multiple and tedious steps [19–21]. Among them, Ru-based NPs have been identified as one of the most effective catalysts toward hydrolysis of AB. To this end, numerous efforts have been developed to increase the catalytic activity and stability of the Ru NPs by using different supports. Fan reported Ru NPs supported on g-C_3N_4 with TOF of 313 min^{-1} [22]; Rakap reported RuPt NPs supported on poly(N-vinyl-2-pyrrolidone) (PVP) with TOF of 308 min^{-1} [23]; Fernandes reported Ru NPs supported on carbon thin firm with TOF of 70.5 min^{-1} [24]; Özkar's group reported Ru NPs supported on nano-TiO_2, magnetic silica coated cobalt ferrit, and xonotlite nanowire with TOF of 241 [25], 172 [26], and 135 min^{-1} [27] respectively; Yao reported Ru NPs embedded on SiO_2 with TOF of 200 min^{-1} [28]; our group reported Ru NPs embedded on MIL-101 with TOF of 178 min^{-1} [29]. In the light of previous works about the effects of morphology of Ru NPs and supported materials, the ultrafine Ru NPs with a narrow size distribution and high dispersion may be conductive to their catalytic performance. Recently, our group have synthesized Ru/graphene via a one-step procedure using methylamine borane as reducing agent in aqueous at room temperature [30]. Compared with $NaBH_4$ and ammonia borane, the Ru/graphene reduced by weaker reducing agent methylamine borane has the smallest size and highest catalytic activity. However, some of the Ru NPs have already aggregated as indicated by transmission electron microscopy (TEM). Herein, we designed a facile improved "one-pot" approach to prepare graphene supported monodisperse Ru NPs with narrow size distribution in ethylene glycol using ascorbic acid as reducing agent. The as-synthesized catalysts exert improved catalytic activity toward the hydrolytic dehydrogenation of AB under ambient temperature, with the turnover frequency (TOF) value is 600 mol H_2 min^{-1} (mol Ru)$^{-1}$, which is among the highest value ever reported.

Experimental

Chemicals

Ammonia borane (NH_3BH_3, AB, Aldrich, 90%), sodium borohydride (Sinopharm Chemical Reagent Co., Ltd., ≥96%), potassium permanganate ($KMnO_4$, Shanghai Chemic Co., Ltd., ≥99.5%), hydrogen peroxide (H_2O_2, Sinopharm Chemical Reagent Co., Ltd., ≥30%), sulfuric acid (H_2SO_4, Sinopharm Chemical Reagent Co., Ltd., 95–98%), phosphoric acid (H_3PO_4, Sinopharm Chemical Reagent Co., Ltd., ≥85%), graphite power (Sinopharm Chemical Reagent Co., Ltd., ≥99.85%), ascorbic acid ($C_6H_8O_6$, Sinopharm Chemical Reagent Co., Ltd., ≥99.7%), ethylene glycol ($C_2H_6O_2$, Sinopharm Chemical Reagent Co., Ltd., ≥99%), ruthenium chloride hydrate ($RuCl_3 \cdot nH_2O$, The Wuhan Xinsirui Technology Co., Ltd., ≥99.9%). All chemicals were used as obtained. We use ordinary distilled water as the reaction solvent.

Characterization

TEM images were obtained using a FEI Tecnai G20 U-Twin TEM instrument operating at 200 kV. Powder X-ray diffraction (XRD) patterns were measured by a Bruker D8-Advance X-ray diffractometer using Cu Ka radiation source ($\lambda = 0.154178$ nm) with a velocity of $6°$ min^{-1}. FTIR spectra were collected at room temperature by using a Thermo FTIR-iS10 instrument using KBr discs in the 400–4000 cm^{-1} region. Raman spectra were carried out using a confocal Raman microscope (Renishaw, RM-1000) at 514.5 nm excitation. Elemental composition was determined by an inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was performed on IRIS Intrepid II XSP. X-ray photoelectron spectroscopy (XPS) measurement was performed with a Kratos XSAM 800 spectrophotometer.

Graphite oxide (GO) preparation

Here we use an improved method, a 9:1 mixture of concentrated H_2SO_4/H_3PO_4 (360:40 mL) was added to graphite flakes (3.0 g, 1 wt equiv). Under continuous stirring, $KMnO_4$ (18.0 g, 6 wt equiv) was added partially to prevent the temperature of the reaction from increasing too high. The reaction was then heated to 50 °C and stirred for 12 h. The reaction was cooled to room temperature and poured into the mixture of deionized water (400 mL) and 30% H_2O_2 (3 mL) which was placed into the ice-bath. The resultant solution was centrifuged to obtain the product. Centrifuged product was then washed in succession with 200 mL of water, 200 mL of 30% HCl, 200 mL of ethanol and dried under vacuum at 25 °C.

Synthesis of Ru/graphene catalysts

5 mg $RuCl_3$ and 50 mg GO were dispersed in 10 mL ethylene glycol. 100 mg ascorbic acid as reducing agent was added to the mixture, ultrasonication was necessary to get a uniform dispersion. Then the mixture was transferred into a well-sealed autoclave with a Teflon liner of 20 mL capacity. The autoclave was slowly heated up to 453 K at a rate of 2 K min^{-1} and kept at this temperature for 5 h. After the autoclave was air-cooled down to room temperature naturally, ethanol was added to precipitate the nanoparticals, and the product was collected by centrifugation at 8500 rpm for 10 min. The obtained NPs were further washed twice in ethanol and dried by oil pump vacuum at 50 °C for 3 h to give Ru/graphene as a dark gray powder. The ruthenium content of the as-prepared catalyst was determined by ICP-AES as 2 wt%.