

Short communication

Highly stable and sub-3 nm Ni nanoparticles coated with carbon nanosheets as a highly active heterogeneous hydrogenation catalyst

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ABSTRACT

An efficient catalyst of Ni/C hybrid nanosheets was prepared via a facile and simple procedure. The highly dispersed and sub-3 nm Ni nanoparticles (NPs) were coated with the carbon nanosheets which can prevent the aggregation and growth of the Ni NPs. The Ni/C hybrid nanosheets exhibited high activity for the catalytic reduction of 4-nitrophenol (4-NP), which was much higher than many noble metal NPs. Additionally, the magnetic Ni/C hybrid nanosheets showed good separation ability and reusability.

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1. Introduction

In recent years, catalysts based on Ni nanoparticles (NPs) have attracted especially interesting because of their high catalytic activity, high selectivity and good separation ability in hydrogenation reactions.^[1–5] However, Ni NPs tend to aggregate due to their high surface energy and magnetic properties, resulting in a remarkable reduction in their catalytic activities. The intrinsic properties of metal NPs are mainly determined by their size, shape, composition, crystallinity, and structure.^[6–9] In principle, one could control one or more of these parameters to fine-tune the properties of the NPs. It is reported previously that if the size of Ni NPs can be controlled below 5 nm, the coking process can be effectively impeded, thus slowing down the deactivation process^[10]. Therefore, lots of attention has been paid on developing new approaches to prepare Ni NPs with controllable size and excellent stability. For instance, Zhang and co-workers have immobilized Ni NPs to mesoporous silica. The pore walls prevented the sintering of Ni NPs, thus achieving catalysts with improved performance^[11]. Both Liu and Wang's groups have confirmed that the performance of Ni-based catalyst can be improved owing to the decrease of the Ni grain size^[12,13]. However, it is still a challenge work to prepare the ultrafine and stable Ni NPs.

Carbon materials have been considered as excellent supports due to their intrinsic properties such as high surface area, unique electronic

properties and chemical inertness as well as thermal stability and high mechanical strength^[14–20]. Thus far, various carbon-based hybrid nanostructures have been reported to exhibit high catalytic performance in either high activity or good stability. However, commonly, the preparation of carbon-based hybrid nanostructures by methods described in the literature is time consuming and relatively expensive due to its complex procedure^[15,21]. Besides, the NPs prepared by the methods are difficult to obtain the desired size and morphology^[22,23]. On the basis of the previous reports, an ideal carbon-based Ni hybrid nanostructure that combines key aspects of the catalyst including high activity, structural and phase stability, and easiness in preparing is highly anticipated.

Recently, Hyeon's group has developed a melting salt method for the preparation of ferrite/carbon hybrid nanosheets^[24]. In this work, sub-3 nm Ni NPs coated with carbon nanosheets were prepared by a simple and straightforward procedure without any separate assembly process. The carbon nanosheets can prevent the aggregation and growth of the ultrafine Ni NPs. When the as-prepared Ni/C hybrid nanosheets were applied in the reduction of 4-nitrophenol (4-NP), they performed excellent catalytic activity as well as recoverability and recyclability. 4-NP is a major class of environmental contaminants, while the reduction product of 4-aminophenol (4-AP) has been used as an important intermediate in the preparation of chemical products^[25–28]. The excellent catalytic performance of the Ni/C hybrid nanosheets can be attributed to the ultrafine size of Ni NPs and the unique structure of the catalyst, which can retain the mechanical integrity during catalytic reaction. It is envisioned that the current reaction strategy can be a guide to these metal NPs coated with carbon for their catalytic application.

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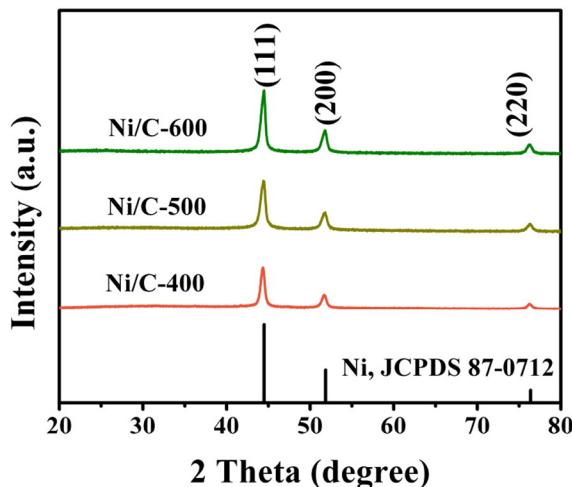


Fig. 1. XRD patterns of the as-prepared Ni/C-400, Ni/C-500 and Ni/C-600.

2. Experimental section

2.1. Synthesis of Ni/C hybrid nanosheets

In a typical procedure, 1 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2 mmol of NaOA were added to the solution containing 10 mL of deionized water, 20 mL of absolute ethanol and 30 mL of hexane. The mixed solution was stirred at 70 °C for 30 min until the nickel ions were transferred from the lower aqueous solution to the upper organic phase. Then 2 mmol of NaOH was added to the solution and the mixture solution was stirred for 4 h. After cooling down to room temperature, the upper organic phase was separated and dried to remove hexane. The obtained precipitation was mixed with a template of Na_2SO_4 (Fig. S1) and ground in a mortar for 30 min to form a fine powder. These results

of Thermogravimetry analyses (TGA) indicated that the self-assembled oleate ligands decomposed completely until the thermal temperature reached 400 °C (Fig. S2). Therefore, the mixture was heated to a target temperature (400 °C, 500 °C, 600 °C and 700 °C) at a heating rate of 10 °C·min⁻¹ under argon (Ar) atmosphere and then kept at that temperature for 3 h. After cooling down, the product was washed with deionized water and dehydrated in a laboratory scale freeze dryer. Then the Ni/C hybrid nanosheets were obtained.

2.2. Catalytic reduction of 4-NP

Typically, 2.95 mL 4-NP solution (0.1 mM) and 0.25 mmol NaBH_4 (9.5 mg) were added in a standard quartz curette. The color of the solution immediately turned from light yellow to bright yellow after NaBH_4 was added. Subsequently, Ni/C catalyst (50 μL , 1 mg/mL) was added to the bright yellow solution. The color of the solution vanished, indicating the reduction of 4-NP. Progress of the reaction was determined by UV-vis absorption spectroscopy (Shimadzu UV-2550PC), which was recorded in a scanning range of 250–500 nm at room temperature. For thermodynamic testing, Ni/C catalyst (250 μL , 1 mg/mL) was added in 4-NP solution (0.1 mM, 59 mL) in the presence of excess NaBH_4 and heated using an oil bath. In recycling, the Ni/C hybrid nanosheets were separated with a magnet, washed three times with deionized water and subsequently subjected to the next reaction run. The conversion (%) of 4-NP can be calculated by the following equation:

$$\text{Conversion (\%)} = (C_0 - C_t)/C_0 \times 100\% \quad (1)$$

In which C_0 is the concentration of 4-NP in solution at the initial time and C_t is the concentration of 4-NP in solution at the time t, respectively.

2.3. Characterization

The crystal structure of the samples were determined by X-ray diffraction (XRD, BRUKER D2 with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$)). The

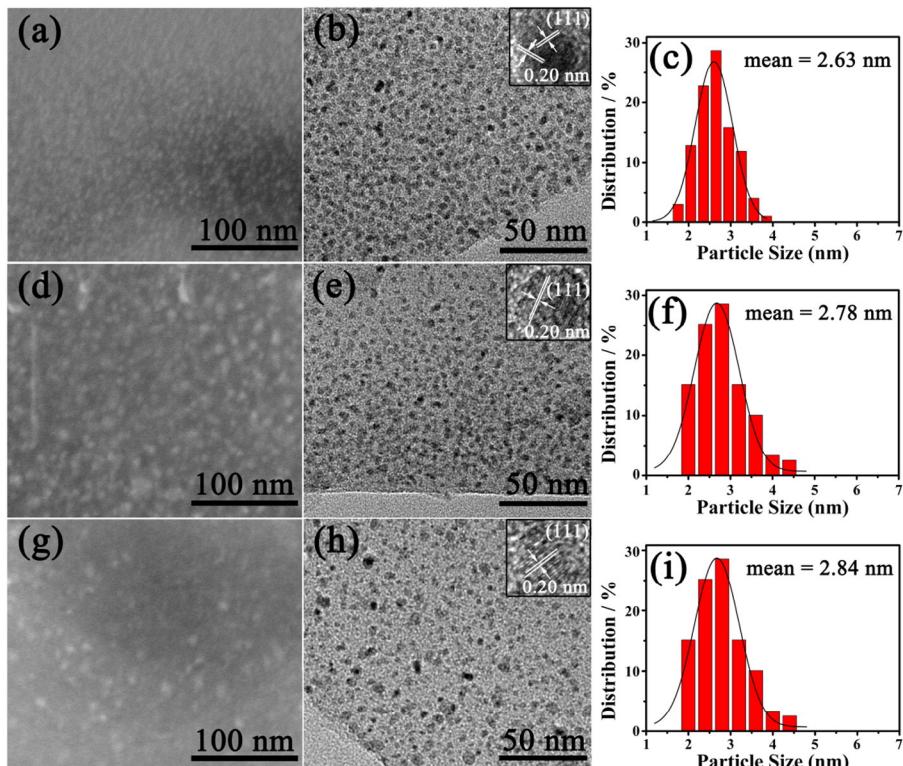


Fig. 2. FESEM images (a, e, g), TEM and HRTEM images (b, e, h) of Ni/C-400, and Ni/C-500 and Ni/C-600 and their relative particle size distribution of Ni NPs (c, f, i).

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