



# Nickel catalyst stabilization via graphene encapsulation for enhanced methanation reaction



Chao Wang<sup>a,b,1</sup>, Peng Zhai<sup>a,1</sup>, Zhichao Zhang<sup>c</sup>, Yi Zhou<sup>a</sup>, Jiakang Zhang<sup>a</sup>, Hui Zhang<sup>d</sup>, Zujin Shi<sup>a,\*</sup>, Ray P.S. Han<sup>b</sup>, Fuqiang Huang<sup>a,d,\*</sup>, Ding Ma<sup>a,\*</sup>

<sup>a</sup> College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China

<sup>b</sup> College of Engineering, Peking University, Beijing 100871, People's Republic of China

<sup>c</sup> Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

<sup>d</sup> Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, People's Republic of China

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## ABSTRACT

Synthesis of chemically stable non-precious-metal 3d-block transition metal nanocatalysts for catalytic syngas conversion remains a great challenge, since the nanocatalysts are usually too active to remain stable under ambient conditions. In situ grown (N-doped) graphene-encapsulated Ni nanoparticles (NPs) (Ni@G, Ni@G-N) were successfully obtained by a simple route via an arc-discharge method. The Ni@G composite is composed of a graphene sheath and a metallic nickel core. The carbon layer can prevent the inner Ni NPs from being etched when they are exposed to air, H<sub>2</sub>O<sub>2</sub> or acid. Moreover, the as-prepared Ni@G exhibit excellent catalytic activity and methane selectivity and high stability in the methanation reaction. The catalytic performance can be further improved by doping nitrogen into the graphene shell. This method provides a good procedure for graphene encapsulation of non-precious-metal nanoparticles.

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## 1. Introduction

In chemical processes, catalysts are able to promote many reactions efficiently. Nanometal catalysts are favorite materials due to the high density of states (DOS) near their Fermi levels [1,2]. Noble metals possess high chemical stability and activity on the nanoscale, and for these reasons they have received enormous attention in practical applications [3]. However, noble metal nanocatalysts are usually scarce and expensive and thus not applicable for all chemical reactions. Therefore, non-precious-metal 3d-block transition metal nanocatalysts (such as Fe, Ni, and Co) become the first choice in chemical processes from economic considerations [4]. Nevertheless, searching for such chemically stable nanoparticles for catalysis and subsequent characterization remains a great challenge, because they are usually too active to remain stable even at room temperature. Metal nanoparticles are reported to be stabilized via surface passivation by coating with organic molecules, polymers, or oxides [5–7]. These electronically poorly conductive coatings may block effective charge transfer between the catalysts

and the reagents, and thus reduce the electrical conductivities and work functions of metal nanoparticles. Therefore these coatings prevent harm to catalytic activity. The ideal passivation layer should not only stabilize metal nanoparticles in the reaction environment, but also maintain their necessary electronic conductivity and chemical activity as catalysts.

Conductive carbon coatings are normally desired, and graphene is the best one with a single atomic layer, which possesses extremely high electron mobility up to 15,000 cm<sup>2</sup> V<sup>-1</sup> s at room temperature [8]. It was reported that it can serve as a passivation layer to prevent 3d-block transition metals (Cu, Ni) from oxidizing due to its diffusion suppression and chemical inertness to oxidizing gases [9,10]. These graphene-coated metal nanoparticles possess a different work function, which makes them available for different specific catalytic reactions [11–13]. It was found that the chemical reactivity of metals encapsulated by carbon nanotubes changed drastically, leading to high activity in redox processes, hydrogen evolution reactions, or dye-sensitized solar cells [14–16]. However, it is difficult for exfoliated graphene (or oxide) sheets to cover metal nanoparticles fully. In situ grown graphene coatings on metal substrates require high temperatures (usually above 800 °C), but metal nanoparticles easily surface-melt and ripen at these high temperatures [17]. Therefore, a novel synthetic route is needed to obtain graphene-coated metal nanoparticles. If Ni

\* Corresponding authors.

E-mail addresses: [zjshi@pku.edu.cn](mailto:zjshi@pku.edu.cn) (Z.J. Shi), [huangfq@pku.edu.cn](mailto:huangfq@pku.edu.cn) (F.Q. Huang), [dma@pku.edu.cn](mailto:dma@pku.edu.cn) (D. Ma).

<sup>1</sup> These authors contributed equally to this work.

metal and carbon can vaporize simultaneously, as in a cloud chamber, graphene-coated Ni nanoparticles can be fabricated. Arc discharge is an easy method to generate high temperatures up to ~5000 K [18] and has long been a popular method of synthesizing various carbon nanomaterials such as fullerenes, carbon nanotubes, and graphene [19–22]. Although metal (e.g., Ti, Fe, Sn, Ge) nanoparticles within carbon nanotubes, graphene, or thick graphitic carbon matrices obtained using the arc discharge method have been reported, the carbon content was usually too high [23–26]. Differently from Ti or Fe metals, which react with carbon to form carbides ( $\text{TiC}_x$ ,  $\text{FeC}_x$ ), Ni, Co, and Cu metals do not react with carbon except to dissolve carbon. These metals are therefore well-known metal substrates for graphene CVD growth [27,28]. Graphene coating is hence relatively easy to achieve on these 3d-block transition metal substrates. For these reasons, it is worth exploring the catalytic performance of these systems.

Conversion of syngas from the gasification of coal or biomass into synthetic natural gas (SNG) via the methanation reaction has recently been proposed as a possible approach to deal with energy problems [29,30]. Ni-based catalysts have been widely employed for methanation reactions due to their low cost, high catalytic activity, and high selectivity [31]. However, current Ni-based catalysts, e.g.,  $\text{Ni}/\text{Al}_2\text{O}_3$ , will lose activity at high temperatures because of the sintering of Ni particles and easy carbon deposition [32–34]. Various supports and promoters have been explored to increase the activity and stability of Ni-based catalysts. However, they can complicate the synthesis by reducing specificity or efficiency [35,36]. Herein, we report a simple one-step route to prepare in situ graphene-encapsulated nickel nanoparticles (Ni@G) via an arc discharge method. The nickel NPs with diameter 5–15 nm are encapsulated by 2–4 layers of graphene. The graphene layer can protect the inner Ni NPs well from oxidizing when exposed to air,  $\text{H}_2\text{O}_2$ , or acid. It is generally believed that the carbon species formed on the nickel surface will lead to severe reduction of activity [37]. However, our as-prepared Ni@G exhibits excellent catalytic activity and methane selectivity and high stability without any support or promoter in the methanation reaction. Moreover, the catalytic performance can be further improved by N-doping in the graphene shell. This approach proves to be a new idea for designing stable nanocatalysts to be used under harsh conditions.

## 2. Experimental

### 2.1. Synthesis of Ni nanoparticles

#### 2.1.1. Synthesis of graphene-encapsulated Ni nanoparticles (Ni@G)

The Ni@G sample was synthesized by an arc discharge method similar to what we reported elsewhere [38]. Typically, DC arc discharge was carried out in a water-cooled stainless steel chamber. The anode was a nickel rod 6 mm in diameter and 140 mm in length while the cathode was a graphite rod 8 mm in diameter. Both electrodes were installed horizontally. The cathode was fixed on a water-cooled copper pedestal. The chamber was first vacuumed to below 10 Pa, and then it was filled with He and  $\text{CH}_4$  (1:2 molar mixture) to a pressure of 0.08 MPa. As the rods were brought close together, an arc discharge occurred, resulting in the formation of plasma. The current was kept at 40 A during the whole process. As the anode was consumed, the rods were kept at a constant distance from each other of about 3 mm by rotating the cathode manually intermittently. The typical synthesis time was about 50 min and about 6 cm of the anode nickel rod was consumed. When the arc discharge was finished, the black soot generated was collected from the chamber wall in ambient atmosphere and conserved in the air. For post-treatment, some part of the as-prepared Ni@G was dipped in 1 mol  $\text{L}^{-1}$  hydrochloric acid with mechanical stirring

at 600 RPM for 12 h. Some part was annealed in air at 200 °C for 2 h and another part was ultrasonically treated with 5%  $\text{H}_2\text{O}_2$  for 1 h.

#### 2.1.2. Synthesis of N-doping graphene encapsulated Ni nanoparticles (Ni@G-N)

The synthesis of Ni@G-N follows procedures similar to those for the Ni@G sample preparation. The anode is also a nickel rod of 6 mm diameter. Differently, the atmosphere is  $\text{CH}_4/\text{NH}_3/\text{He}$  (3:1:2 molar mixture) at a pressure of 0.08 MPa. The current was also kept at 40 A. The typical synthesis time was about 40 min and about 5.5 cm of the anode nickel rod was consumed.

#### 2.1.3. Synthesis of metallic Ni nanoparticles (Ni NPs)

In parallel, the metallic Ni NPs without graphene encapsulation were synthesized by the arc discharge method. Most of the process is similar to that of the Ni@G and Ni@G-N sample. The only difference is the atmosphere, which is He and  $\text{H}_2$  (1:2 molar mixture) at a pressure of 0.08 MPa. The typical synthesis time was about 47 min and about 7 cm of the anode nickel rod was consumed.

## 2.2. Catalyst characterization

The microstructures were studied by transmission electron microscopy (TEM) using a JEM-2100 electron microscope (JEOL Ltd., Japan) working at 200 kV. Powder X-ray diffraction (XRD) patterns were collected at a scanning rate of  $2.4^\circ \text{min}^{-1}$  in the  $2\theta$  range from  $10^\circ$  to  $80^\circ$  on a Bruker D2 Focus diffractometer with monochromatized  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Raman spectra were measured using a Renishaw Raman spectrometer with laser excitation at 532 nm. The BET surface area, pore volume, and average pore diameter of catalysts were measured by nitrogen physisorption at  $-196^\circ \text{C}$  in an ASAP 2020 instrument (Micromeritics, USA). Each sample was degassed under vacuum at  $90^\circ \text{C}$  for 1 h and  $300^\circ \text{C}$  for 4 h prior to measurement. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an Axis Ultra imaging photoelectron spectrometer (Kratos Analytical Ltd.) using a monochromatized  $\text{Al K}\alpha$  anode (225 W, 15 mA, 15 kV), and the  $\text{C}1s$  peak at 284.8 eV was taken as an internal standard. Thermogravimetric analysis (TGA) was carried out on a Q50TGA thermogravimetric analyzer from room temperature to  $900^\circ \text{C}$  at a heating rate of  $10^\circ \text{C min}^{-1}$  in air. Inductively coupled plasma atomic emission spectrometry (ICP-AES) measurements were used to detect the nickel content in the filtrate using a PROFILE SPEC instrument.

CO temperature-programmed desorption (CO TPD) experiments were performed in a U quartz tube flow reactor. Specifically, 50 mg of catalyst was reduced with  $\text{H}_2$  (10 ml/min) at  $500^\circ \text{C}$  for 2 h. After the reduction, the sample was purged with He (40 ml/min) to room temperature. After exposure to CO for 30 min, the catalyst was switched to He exposure until the baseline of the CO signal leveled off. Finally, the temperature was increased to  $400^\circ \text{C}$  at  $10^\circ \text{C/min}$ . The mass signal of 28 was monitored by a quadrupole mass spectrometer (Pfeiffer GSD320).

The Mott–Schottky plots were measured in 0.1 M  $\text{Na}_2\text{SO}_4$  electrolyte at a frequency of 1 kHz using an electrochemical station (CHI660D, Shanghai Chenhua Limited, China) in a conventional three-electrode configuration with the sample spin-dropped on an indium tin oxide (ITO)-coated glass as working electrode, a platinum wire as counter electrode, and a saturation calomel electrode (SCE) as reference electrode. The electrochemical impedance spectroscopy (EIS) plots were measured in the frequency range from 0.01 Hz to 100 kHz.

### 2.3. Syngas methanation reaction tests

The methanation reaction was carried out in a multichannel fixed bed flow reactor (see Fig. S1 in Supplementary Material).

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