

Facile and large-scale synthesis of high quality few-layered graphene nano-platelets via methane decomposition over unsupported iron family catalysts



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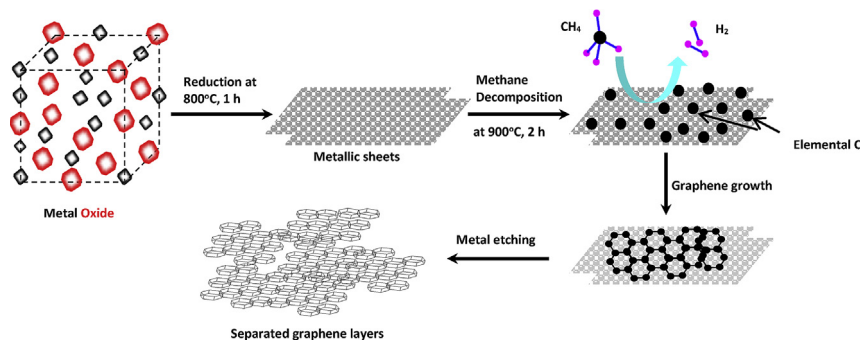
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HIGHLIGHTS

- Few-layered graphene nanoplatelets were prepared via methane catalytic decomposition.
- Metallic sheets of iron group metals were used as novel catalysts.
- The surfaces of metallic sheets were found to be very effective for GNPs growth.
- The number of layers is dependent on the morphological structure of the catalysts.
- The unsupported metallic Ni catalyst exhibited higher catalytic growth activity.

GRAPHICAL ABSTRACT



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ABSTRACT

High quality few-layered graphene nano-platelets (GNPs) were successfully prepared via catalytic chemical vapor deposition of methane under ambient pressure using substrate-free unsupported iron, cobalt, and nickel metallic sheets as catalysts. The bulk catalysts were prepared via combustion method using citric acid as a fuel. Various analytical techniques, including high-resolution transmission electron microscopy (TEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA), temperature programmed reduction (TPR) and Raman spectroscopy were employed to characterize the fresh and reduced catalysts and to identify the morphological structure of the as-grown GNPs. TEM images of the reduced metal catalysts showed that polycrystalline metallic sheets were easily produced after complete reduction of unsupported metal oxides. The data demonstrated that the formation of zero-valent metallic sheets could effectively promote the growth of GNPs on their surfaces. The unsupported Ni catalyst exhibits higher catalytic growth activity in terms of GNPs yield (254 wt%) compared with all other catalysts. Raman spectra and TEM results established that a few layers of GNPs with high crystallinity and good graphitization were produced. TGA results further demonstrated that the as-grown GNPs exhibit significantly higher thermal stability in air atmosphere compared with other synthesis methods.

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1. Introduction

Graphene is a two-dimensional material composed of a flexible sheet(s) of carbon atoms that recently has attracted a lot of attention due to its exceptional mechanical, electrical, thermal and optical properties [1]. Graphene nano-platelets (GNPs) are viewed as a promising material for a wide range of important applications, such as energy storage devices [2], field-effect transistors [3,4], nanocomposites and biosensors materials [5–7], catalysis [8] and many other applications [9–11]. Accordingly, simple and mass production of high-quality GNPs is an important challenge in order to release its relevant applications.

GNPs can be produced by several methods, including mechanical exfoliation of graphite [12], graphitization of SiC at elevated temperatures (>1200 °C) [13], carbon nanotube unzipping (CNT) [14], chemical exfoliation and reduction of graphite [15–17], and chemical vapor deposition (CVD) of hydrocarbons on a substrate surface [18–25]. The chemical exfoliation method is widely used for large-scale production of graphene, which is usually produced via oxidation of pristine graphite to graphite oxide, exfoliation, and reduction of the obtained graphene oxide to graphene platelets. However, the presence of oxygen functional groups induces structural defects in graphitic layers due to the vigorous oxidation and exfoliation processes; hence, poor quality graphene is typically obtained [26].

Among the different production techniques, the CVD process is considered as a promising approach for fabrication of large scale GNPs with relatively few defects. Also, CVD is the most popular method for synthesis of highly graphitized CNT [27–31]. The catalyst plays an essential role for directing the growth mechanism to either CNT or GNS depending on its composition. This means that catalyst nanoparticles are favored and effective to synthesize the CNT, however, metal foils, in particular copper and nickel, are widely used to synthesize mono- to few-layered graphene platelets [19,21,25,32–35]. This is due to the fact that the shape of the CNT is formed according to the spherical shape of catalyst nanoparticles, whereas a sheet of graphene is synthesized based on the shape of one piece of foil [36].

Although the iron group (Fe, Co and Ni) based catalysts are considered as the most active catalysts for production of carbon nanostructured materials via CVD method, very little citations were reported for the use of these bulk metals [37,38], specifically, in the oxide or metallic forms as catalysts in graphene synthesis. Therefore, we can expect the higher catalytic activity of these unsupported metals for graphene growth by CVD method depending on their texture and morphological properties. In this context, unsupported metallic Fe, Co and Ni catalysts were prepared by combustion method and evaluated as novel catalysts for CVD graphene growth. To the best of our knowledge, the comparison of catalytic growth activity of these metallic catalysts toward synthesis of GNPs by methane thermal decomposition under ambient pressure has not been reported yet in the literature. To the best of our knowledge, the use of metallic cobalt as a catalyst for CVD synthesis of GNPs via methane decomposition has not also been discussed to date.

2. Experimental

2.1. Catalyst preparation

Unsupported bulk iron, cobalt and nickel oxides were prepared via solution combustion method using citric acid as a fuel. Briefly, a desired amount of metal nitrate, i.e., $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, was dissolved with citric acid (molar ratio 1:0.5, respectively) in sufficient quantity of deionized

water to obtain a homogenous mixture. The mixture was then gently evaporated under continuous stirring at -80°C until a paste was obtained. The obtained pastes were calcined in air at 600°C for 3 h to form the metal oxide catalyst.

2.2. Production of GNPs

Powder X-Ray diffraction (XRD) pattern of calcined, reduced, and used catalysts were conducted using a Philips X-pert diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$) in the 2θ range of $10\text{--}90^\circ$. The crystallite size of the oxide and metallic forms of the metals were calculated by Scherrer's equation using full width half maximum of the XRD peak.

Temperature programmed reduction (TPR) analysis was carried out in a quartz reactor under $10\% \text{H}_2/\text{N}_2$ flow (50 ml/min) from ambient temperature to 900°C at a heating rate of $4^\circ\text{C}/\text{min}$. Hydrogen consumption was monitored by an on-line gas chromatograph (Perkin Elmer's Clarus 600 Gas Chromatograph, USA) equipped with thermal conductivity detector to monitor the H_2 concentration.

The morphology and structure of reduced catalysts, as well as the as-grown GNPs were characterized via high-resolution transmission electron microscopy (HR-TEM), model JEM-200CX, JEOL, Japan. A small quantity of the sample was dispersed in ~ 10 ml ethanol then sonicated for 10 min. Few drops of the suspension were placed on a covered copper grid and photographed.

Thermogravimetric analysis (TGA) of as-synthesized GNPs was conducted using SDT; Q600 apparatus with 20 mg samples at a heating rate of $10^\circ\text{C}/\text{min}$ in an air flow of $50 \text{ cm}^3/\text{min}$. The GNPs yield was calculated according to the following equation:

$$\text{GNPs yield (\%)} = (\% \text{ of weight loss by carbon oxidation} / \% \text{ of residue left after oxidation}) \times 100$$

Raman spectroscopic analysis was performed at room temperature using SENTERRA Dispersive Raman Microscope (Bruker) equipped with a diode Nd:YAG laser and a wavelength of 532 nm from frequencies of $500\text{--}3000 \text{ cm}^{-1}$.

2.3. Materials characterization

The catalytic growth of GNPs has been carried out at 900°C under atmospheric pressure using a horizontal fixed bed quartz flow reactor with an inner diameter of 25 mm and 1000 mm length. A catalyst weight of 250 mg was located at the center of quartz reactor. Prior to the reaction, the catalyst was reduced in situ at 800°C for 1 h using undiluted hydrogen with a flow rate of 50 sccm (standard cubic centimeter per minute). The reactor was then heated to the prescribed reaction temperature of 900°C under N_2 flow of 60 sccm. After equilibration, the feed was switched to a mixture of CH_4 and N_2 , with flow rates of 45 and 60 sccm, respectively, and continued for 2 h. Finally, the reactor was cooled down to room temperature at ambient rate under N_2 flow of 100 sccm.

3. Results and discussion

3.1. Characterization of unsupported oxide and reduced Fe, Co and Ni catalysts

The XRD patterns of freshly unsupported Fe, Co and Ni oxides after calcination in air at 600°C for 3 h are displayed in Fig. 1a–c. It is observed that the diffraction peaks of all metal oxides are significantly sharp, revealing good crystallinity. As illustrated in Fig. 1a, the diffraction peaks at 2θ of 37° , 43° , 62° , 75° and 79° are

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