Plasma assisted fabrication of multi-layer graphene/nickel hybrid film as enhanced micro-supercapacitor electrodes

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Abstract. A facile synthesis strategy has been developed for fabricating multi-layer graphene/nickel hybrid film as micro-supercapacitor electrodes by using plasma enhanced chemical vapor deposition. The as-presented method is advantageous for rapid graphene growth at relatively low temperature of 650 °C. In addition, after pre-treating for the as-deposited nickel film by using argon plasma bombardment, the surface-to-volume ratio of graphene film on the treated nickel substrate is effectively increased by the increasing of surface roughness. This is demonstrated by the characterization results from transmission electron microscopy, scanning electron microscope and atomic force microscopy. Moreover, the electrochemical performance of the resultant graphene/nickel hybrid film as micro-supercapacitor working electrode was investigated by cyclic voltammetry and galvanostatic charge/discharge measurements. It was found that the increase of the surface-to-volume ratio of graphene/nickel hybrid film improved the specific capacitance of 10 times as the working electrode of micro-supercapacitor. Finally, by using comb columnar shadow mask pattern, the micro-supercapacitor full cell device was fabricated. The electrochemical performance measurements of the micro-supercapacitor devices indicate that the method presented in this study provides an effective way to fabricate micro-supercapacitor device with enhanced energy storage property.

Keywords: plasma enhanced chemical vapor deposition, graphene; thin film, micro-supercapacitor

1. Introduction
As a kind of energy storage devices with high power density, high efficiency, long life expectancy and environmental friendliness, supercapacitors have received considerable research attention for the past two decades [1, 2]. Moreover, due to the increasing needs of small-scale energy storage units within the micro/nanosystems of electronic devices, the studies about micro-supercapacitors have become
focus topics in recent years [3, 4]. In general, based on the electrical double layer energy storage mechanism, carbon-based materials have been approved as the promising candidates for electrode materials in supercapacitor applications [5, 6]. Recently, different types of carbon-based materials, such as activated carbons, carbon nanotubes (CNTs) and graphene, have been employed to fabricate high performance micro-supercapacitor electrodes [7-12]. As a two-dimensional material with atomic thickness, graphene has attracted significant attention for use as supercapacitor electrodes, owing to its unique structure and physical behaviors, such as large surface area and high in-plane electrical conductivity [11-14]. In addition, due to the requirement of microelectrodes with two-dimensional permeable channels, graphene sheets are ideally suitable to fabricate micro-supercapacitor electrodes, which can be integrated on a substrate [15, 16].

For the synthesis of graphene, mechanical exfoliation, chemical exfoliation, epitaxial growth over SiC, and chemical vapor deposition (CVD) are mostly used methods [17-26]. Comparing with other methods, the CVD technique is mostly promising for large-scale graphene growth and meets the projected demand of graphene production for its single-step process [27, 28]. Metallic substrate, which is commonly copper (Cu) or nickel (Ni), is essential in the CVD method because it would decrease the decomposition energy of raw reactants [29, 30]. However, the synthesis temperature of graphene by using CVD method is relatively high, while the consuming time of graphene growth by using CVD method is relatively long [31, 32]. Therefore, for large-scale applications of graphene materials on micro-supercapacitors, there is still a challenging to develop a simple and effective method for synthesizing graphene sheets at relatively low temperature. Since plasma energy could effectively help to dissociate hydrocarbons, plasma enhanced CVD (PECVD) technique has been widely utilized for low temperature preparation of graphene sheets (graphene layer >3 layers) with reasonable growth rates [33, 34].

However, micro-supercapacitors made of conventional graphene electrodes exhibit limited specific capacitance due to the ultra flat surface of graphene films. Since the surface-to-volume ratio for the electrode of micro-supercapacitors is the essential parameter related to the specific capacitance, considerable efforts should be made to increase the surface roughness of the as-prepared graphene films in order to improve the specific capacitance of micro-supercapacitors.

Thus, in this study, the graphene film is grown on the Ni film deposited on the SiO2/Si substrate by using PECVD method. In order to increase the surface roughness, the as-deposited Ni film is pre-treated by using argon (Ar) plasma bombardment to form the rough surface. As a result, the as-synthesized graphene film on the plasma treated Ni film could correspondingly have rough surface. The electrochemical performances of the graphene synthesized by PECVD method are investigated, demonstrating that the graphene/Ni hybrid film with high surface roughness exhibits the expected higher specific capacitance.

2. Experimental

2.1. Chemicals
Iron trichloride (FeCl3), sodium sulfate (Na2SO4) and poly (ethylene oxide) (PEO) are purchased from Sigma-Aldrich Company.

2.2. Preparation of Ni film
In this study, there were two types of Ni film which was deposited on the SiO2/Si substrate. One type of Ni film was deposited on the SiO2/Si substrate by using electron beam evaporation (EB500-I, Shenyang Scientific Instrument Limited, China). On the other hand, to create the rough surface, the as-deposited Ni film was further conducted by Ar plasma treated at 250 W for 35 min. The thicknesses of all of the as-prepared Ni films were 150 nm.

2.3. Synthesis of graphene/Ni hybrid film
In a typical synthesis procedure according to the previous reports [35], the graphene was synthesized by using PECVD (400 model, Shenyang Scientific Instrument Limited, China) on the as-prepared Ni film. The as-prepared Ni films were placed inside the PECVD system chamber. After placing the Ni films inside the PECVD chamber, the base pressure of the PECVD system vacuum chamber was pumped down to $8.5 \times 10^{-4}$ Pa. Then, hydrogen gas ($H_2$) was piping into the chamber at the flow rate of 80 mL min$^{-1}$, and then the Ni films were preheated at 650 °C for 40 min at a pressure of 220 Pa. After this process, the mixed gases with $H_2$, Ar and methane (CH$_4$) were piped into the chamber at the flow rate of 4, 80 and 160 mL min$^{-1}$, respectively. The pressure of vacuum was fixed at 250 Pa. Finally, graphene was synthesized by applying radio frequency power of 200 W on the Ni films at the temperature of 650 °C for 200 s. After turning off the radio frequency power, the heater and CH$_4$ gas were correspondingly shut down. In order to cool down the reaction system, Ar and H$_2$ were kept flowing into the chamber at the rate of 160 and 80 mL min$^{-1}$, respectively. In this study, the two types of graphene/Ni hybrid film, which were made from graphene film grown on the Ni film and the plasma treated Ni film, were named as sample 1 and sample 2, respectively.

2.4. Characterization
To evaluate the quality of the as-prepared graphene, the transfer of graphene was conducted by dissolving Ni film in 1 M FeCl$_3$ solution, followed by rinsing graphene with de-ionized (DI) water for 3 times. And then graphene was transferred to SiO$_2$/Si substrate for further characterization. The morphology and structure of the as-prepared graphene was studied by using transmission electron microscopy (TEM; JEM-2100 JEDL). In addition, the surface morphology of the hybrid film of sample 1 and 2 was characterized by using field-emission scanning electron microscope (FESEM; X-650 HITACHI) and atomic force microscopy (AFM; 5600LS Agilent). Raman spectra of the as-prepared graphene were acquired by using inVia Renishaw Raman Microscope with 532 nm laser radiation source.

2.5. Electrochemical measurement the graphene/Ni hybrid films
Electrochemical behaviors of the graphene/Ni hybrid films as electrodes in micro-supercapacitor were investigated. Both of the two kinds of as-fabricated graphene/Ni hybrid film were used as working electrodes of micro-supercapacitor. In addition, a Pt foil and saturated calomel electrode (SCE) were used as the electrolyte, counter electrode, respectively. A series of electrochemical measurements of the as-fabricated graphene/Ni hybrid films were tested, including the galvanostatic charge-discharge and cyclic voltammetry (CV), by using a three-electrode compartment on a CHI660D Electrochemical System with 1 M Na$_2$SO$_4$ aqueous solution as the electrolyte. Nitrogen gas (N$_2$) was pushed into the electrolyte solution to remove oxygen (O$_2$) in DI water.

2.6. Electrochemical measurement the micro-supercapacitor device
By using the same procedure of synthesizing sample 2, the micro-supercapacitor device was fabricated. In particular, the Ni film was deposited on the SiO$_2$/Si substrate by using electron beam evaporation with comb columnar shadow mask pattern. Then as-fabricated comb columnar Ni film was further conducted by Ar plasma treated at 250 W for 35 min. Finally, the graphene film was grown on the surface of Ni film by using the same procedure mention above. The as-fabricated comb columnar electrode was shown in figure 1. The gel electrolyte used for micro-supercapacitor device encapsulation was made from PEO and Na$_2$SO$_4$. Typically, 4 g PEO was dissolved into 50 mL Na$_2$SO$_4$ solution of 1 M. After stirring for a while, the syrupy gel electrolyte was formed. The as-fabricated comb columnar electrode was encapsulated by using polymethyl methacrylate (PMMA) cap with gel electrolyte inside the cap. Then, a series of electrochemical measurements of the encapsulated micro-supercapacitor device were tested, including the galvanostatic charge-discharge and CV, by using CHI660D electrochemical system.
3. Results and discussions

3.1. Characterizations of graphene

Figure 2 shows the Raman spectra of graphene transferred from the as-prepared two types of Ni film onto SiO₂/Si substrate, where a and b represent graphene sheets from sample 1 and sample 2, respectively. As shown in figure 2, there are three characteristic bands of graphene materials in both Raman spectra of a and b, which are the D band (1350 cm⁻¹), G band (1580 cm⁻¹) and 2D band (2700 cm⁻¹). The intensity ratio between D and G band (I_D/I_G ratio) in Raman spectra of a and b are 1.6 and 1.9, respectively, which indicates that the defect degree of graphene grown on plasma treated Ni film is higher than that of graphene grown on the non-deposited one [36, 37]. Since the pits on the as-deposited Ni film are formed after plasma treating, the as-formed pits are turned into the nucleation center of graphene and prevent the movement of carbon atoms on the surface of Ni film. As a result, the number of graphene flakes tends to be increased, while the edges of these flakes attributed to the high disorder structure. Therefore, it can be concluded that a rougher surface of Ni film could increase the defect degree of graphene films grown on it. To further estimate the surface morphology of graphene sheets from sample 1 and 2, TEM observation is conducted. As shown from the typical TEM images in Figure 3, the as-prepared graphene sheets from sample 1 have flat surface while the as-prepared graphene sheets from sample 2 have rough surface. In addition, from the high resolution TEM in Figure 3, there are crystallized carbon structure with typical interlayer spacing of 0.34 nm in both two graphene samples, which is closely matched with the (002) lattice spacing of graphene [38, 39].

![Figure 1. Schematic diagram of the top view (a) and the side view (b) of the as-fabricated micro-supercapacitor device with comb columnar electrode.](image)

![Figure 2. Raman spectra of graphene sheets obtained from sample 1 (a) and sample 2 (b) [35].](image)
3.2. Characterizations of the as-fabricated electrodes

Since electrochemical measurements are conducted on the electrodes fabricated by using the graphene films on the Ni films, the surface morphology of the final electrode was investigated by using SEM and AFM. By comparing the SEM images of sample 1 and 2 in Figure 4, the black dots in Figure 4 (b) indicate that there are obvious pits on the surface of sample 2, while the surface of sample 1 is flat. Furthermore, the cross section view of the hybrid film in the inset images of Figure 4 (b) indicates the surface roughness of sample 2, which shows the up and down pits on the surface. In addition, as shown in Figure 5, a homogeneous film of sample 1 with a tiny roughness on the surface is observed, while the surface of sample 2 is rougher due to the plasma treated of Ni film. In addition, from the three dimension (3D) view of sample 1 and 2, which is shown in Figure 5 (c) and (d), respectively, sample 2 displays sharper surface in 3D view of AFM images. The morphology of the ups and downs of sample 2 agrees well with the TEM result in Fig 3 (b), which indicates that the graphene films grown on the plasma treated Ni film have rough surface with more pits.

Figure 3. Typical TEM images of graphene sheets obtained from sample 1(a) and sample 2(b) [35]. The inset shows corresponding high resolution TEM image.

Figure 4. SEM images of sample 1(a) and sample 2(b) [35]. The inset shows the corresponding cross section images, where the scale bar is 1 μm.
CV and galvanostatic charge-discharge measurements are used to investigate the capacitive performances of sample 1 and sample 2 as the working electrode of micro-supercapacitors in 1 M Na$_2$SO$_4$ solution. The electrochemical performances are characterized by using a three-electrode configuration. Figure 6 (a) and (b) show the CV curves for sample 1 and sample 2 as the working electrodes under different scan rates from 1 to 100 mVs$^{-1}$, respectively. The exhibition of quasi-rectangular CV curves in the potential window of -0.3-0.7 V demonstrates that the excellent reversibility of the as-synthesized micro-supercapacitor electrodes [40, 41]. Moreover, a higher current density is observed in Figure 6 (b) than that in Figure 6 (a), suggesting that specific capacitance of sample 2 is higher than that of sample 1. The higher specific capacitance of sample 2 is further confirmed by the galvanostatic charge discharge profiles in Figure 6 (c), which are obtained at the current density of 0.5 Am$^{-2}$. As shown in Figure 6 (c), the nearly linear profile and rather symmetric shapes imply that the as-fabricated hybrid films demonstrate the typical double layer capacitive behavior and excellent electrochemical reversibility [42, 43]. Besides the galvanostatic charge discharge behavior of sample 1 and 2 at current density of 0.5 Am$^{-2}$, the charge storage capacity of the as-fabricated two types of electrode is further evaluated by the specific capacitance value obtained from galvanostatic charge discharge test at different current density. As shown in Figure 6 (d), the overall specific capacitance of sample 2 is higher than that of sample 1 at each scan rate, which is due to the larger surface-to-volume ratio of graphene provided by the plasma treated Ni film with rough surface. At low current density of 0.1 Am$^{-2}$, the specific capacitances of sample 1 and sample 2 as the working electrode are 0.5 and 9 Fm$^{-2}$, respectively. Even at the current density of 2 Am$^{-2}$, the specific capacitances of sample 1 and sample 2 are 0.45 and 2.6 Fm$^{-2}$, respectively. Based on the analysis above, the graphene/Ni hybrid film with a rough surface gives rise to about 10 times enhancement of specific capacitance due to the increasing of surface-to-volume ratio. This enhancement indicates that...
the synthesis method mentioned in the present work provides a facile and effective way to fabricate micro-supercapacitor electrodes.

![Figure 6](image_url)

**Figure 6.** Electrochemical behavior of the micro-supercapacitor electrode made of the as-fabricated graphene/Ni hybrid film. (a) CV curves of the micro-supercapacitor electrode made of sample 1; (b) CV curves of the micro-supercapacitor electrode made of sample 2; (c) galvanostatic charge-discharge of the micro-supercapacitor electrode at a current density of 0.5 Am\(^{-2}\); (d) variation in specific capacitance for the micro-supercapacitor electrode against different current densities.

3.3. **Electrochemical behavior of the micro-supercapacitor device**

To further investigate the electrochemical performance of the as-obtained graphene/Ni hybrid film in a full symmetrical cell, micro-supercapacitor device based on sample 2 with comb columnar electrodes were fabricated and shown in Figure 7 (a). Due to the advantages of easy fabrication and wide working temperature, gel electrolyte of PEO/Na\(_2\)SO\(_4\) system was used in the micro-supercapacitor device package. As shown in Figure 7 (b), the as-obtained micro-supercapacitor device exhibits quasi-rectangular CV curves at various scan rates from 1 to 100 mVs\(^{-1}\) a potential window range from -0.3 to 0.7 V, which indicates the fast charge transfer between the electrodes and typical double layer electrochemical behavior. According to Figure 7 (c), the galvanostatic charge discharge curve with a linear and symmetrical shape at the current density of 0.1 Am\(^{-2}\) indicates the capacitor-like characterizations of the as-obtained micro-supercapacitor device. In addition, the micro-supercapacitor device shows a specific capacitance of 0.114 Fm\(^{-2}\) at 0.1 Am\(^{-2}\), and maintains 90% of this value when operated at current density of 1 Am\(^{-2}\), which is shown in Figure 7 (d). Due to the low ionic conductivity of the gel electrolyte utilized in this work, the specific capacitance of the as-fabricated micro-supercapacitor device is unexpected considerable. Nevertheless, the synthesis method in this study provides one effective way to fabricate micro-supercapacitor devices with improved capacitance.
In addition, some ionic liquid or organic electrolytes are attempted to be employed in the future to optimize the performance of the micro-supercapacitor devices.

Figure 7. (a) Digital photograph of the as-fabricated micro-supercapacitor device. (b) CV profiles of micro-supercapacitor device at various scan rates from 1 to 100 mVs\(^{-1}\). (c) galvanostatic charge-discharge curve of micro-supercapacitor device at the current density of 0.1 Am\(^{-2}\). (d) specific capacitance of micro-supercapacitor device obtained from different current densities.

4. Conclusions
In summary, graphene with multi layers is successfully synthesized on Ni film by using PECVD. In addition, the surface of the as-synthesized graphene/Ni hybrid film is tuned by using Ar plasma, giving rise to generate rough surface with improved surface-to-volume ratio. It is found that the electrochemical properties of graphene/Ni hybrid film with rough surface are dramatically improved. When the graphene/Ni hybrid film with improved surface-to-volume ratio is used as the electrode in micro-supercapacitor, the specific capacitance is 10 times higher than the untreated graphene/Ni film. Furthermore, the electrochemical performance of the micro-supercapacitor device with comb columnar electrodes shows that the synthesis method presented in this work provides an effective way to fabricate micro-supercapacitor devices and can be served as guidance for the future design of high performance micro-supercapacitor devices.

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