

# Preparation of graphene nanowalls on nickel foam as supercapacitor electrodes

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Graphene nanowalls (GNWs) were deposited on the surface of the copper foil, nickel foam and glass using the plasma-enhanced chemical vapour deposition (13.56 MHz) method. The etching effect of hydrogen on the morphology of the GNWs was investigated by varying the CH<sub>4</sub>/H<sub>2</sub> ratio during the graphene growth. Supercapacitor electrodes made of GNWs on nickel foam were tested with cyclic voltammetry and galvanostatic charge/discharge methods, showing premium electrical double-layer performance and cyclic stability.

**1. Introduction:** Graphene nanowalls (GNWs) are a new member of the few-layer-graphene family in which the graphene sheets stand vertically on the substrates. Owing to the vertically orientated sheets, GNWs present several unique features such as abundant open-edges and high specific-surface-area and show great potential in a variety of applications [1–6]. Specially, lots of studies focused on fabricating supercapacitor electrodes with GNWs grown on conducting substrates [5–8]. It was an obvious advantage that the conducting substrates acted as the current collectors, omitting the transfer and coating procedures in the traditional methods. Zhao *et al.* reported that the electrodes made of GNWs on carbon paper showed a capacitance of 0.076 F cm<sup>-2</sup> [7]. In Shuai's work, GNWs grown on nickel foil exhibited a high capacitance of 147 F g<sup>-1</sup> [6]. The morphology of GNWs played a critical role in its supercapacitive performance. However, only a few works studied the etching effect of hydrogen on the GNWs' morphology [4]. What's more, these previous researches were limited to the GNWs grown on the two-dimensional substrate; electrodes made of GNWs grown on three-dimensional substrates had never been reported. In this Letter, we investigated the etching effect of hydrogen on the growth of GNWs. Moreover, GNWs were fabricated on the surface of nickel foam and showed a good double-layer-capacitor behaviour.

## 2. Experimental methods

**2.1. Growth of GNWs:** GNWs were deposited in a home-built remote radiofrequency plasma-enhanced chemical vapour deposition (PECVD) system. Copper foil, nickel foam, and glass were used as substrates. Before loading into the quartz tube furnace, the substrates were cleaned with acetone and ethanol. Prior to growth, the furnace was evacuated down to a pressure of 1 × 10<sup>-1</sup> Pa, then the substrates were heated to 600°C at a rate of 10°C/min under the protection of Ar flow of 200 sccm. Thereafter, a mixture flow with different CH<sub>4</sub>/H<sub>2</sub> ratios was introduced into the furnace and simultaneously 150 W radiofrequency (RF) was generated. After the growth, the RF and CH<sub>4</sub>/H<sub>2</sub> were turned off and the samples were cooled down naturally to room temperature.

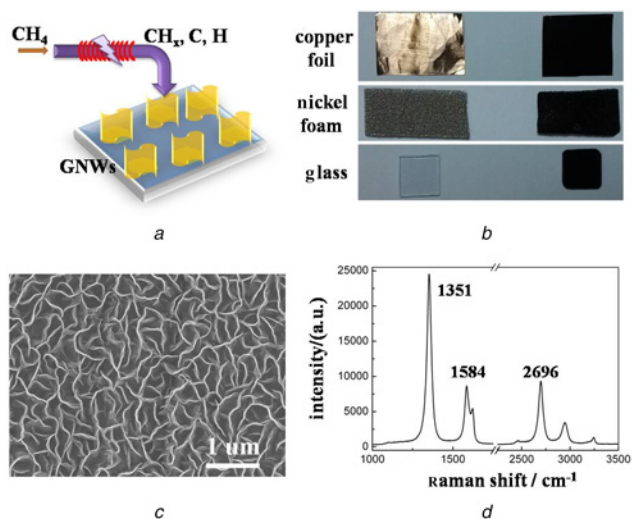
**2.2. Characterisation:** Scanning electron microscopy (SEM) analysis was performed using a Hitachi S-4800 microscope at an acceleration voltage of 10 kV. A Raman spectrum was recorded with a laser wavelength of 532 nm and an incident power of 1 mW (Horiba Jobin Yvon LabRAM HR-800). The Brunauer–Emmet–Teller (BET) specific surface area was determined from

N<sub>2</sub> adsorption by using a Micromeritics ASAP 2460 analyser at liquid nitrogen temperature.

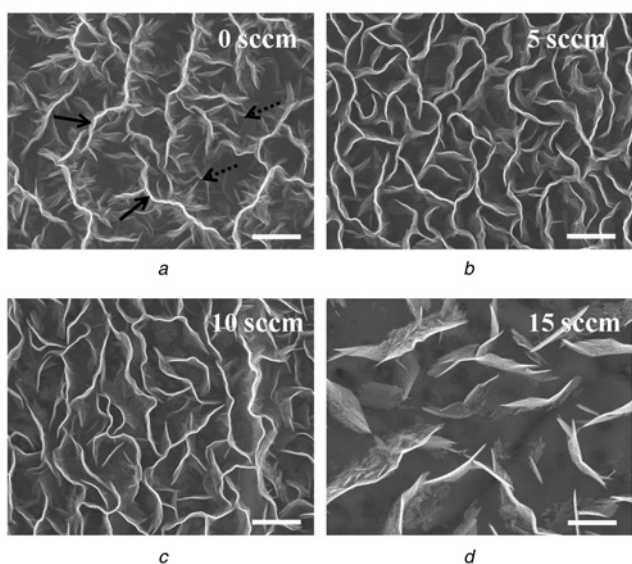
**2.3. Electrochemical measurements:** The cyclic voltammetry (CV) and galvanostatic charge/discharge curves were measured on the CHI 660D electrochemical workstation. A three-electrode system was used with the saturated calomel electrode and the platinum wire as the reference electrode and the counter electrode, respectively. The electrolyte was a mixed solution of 1 M NaAc and 1 M MgSO<sub>4</sub>. All the measurements were carried out at room temperature.

**3. Results and discussion:** Fig. 1*a* shows a schematic illustration of the PECVD apparatus used in our study. The precursor gas was dissociated into active radicals, including CH<sub>x</sub>, atomic C, and H, by the radiofrequency source mounted along the upstream zone of the furnace [2]. These radicals were pumped downstream and self-assembled on the surface of the substrates, forming GNW films. Owing to these radicals created by the radiofrequency, the growth of graphene did not rely on the catalytic activity of metallic substrate, leading to the catalyst-free growth of GNWs on various types of substrates from metals to insulators [2, 9]. The photograph in Fig. 1*b* shows the examples of GNWs grown on three kinds of substrates, copper foil, nickel foam, and glass. It is obvious that the graphene deposition process turned the colour of the surface to black and presented a significant contrast between samples before and after graphene deposition. Fig. 1*c* shows a typical SEM micrograph of GNWs grown on the copper foil, from which we could clearly identify the curled nanowall sheets with an average length of 1 μm. As shown in the Raman spectrum in Fig. 1*d*, three intrinsic peaks located at 1351, 1584, and 2696 cm<sup>-1</sup> provided evidence that the as-grown film was constructed by graphene nanosheets [10, 11].

It is reported that hydrogen played an important role in the growth of graphene. The etching effect of hydrogen could effectively remove the amorphous carbon clusters and improve the quality of graphene [12–14]. In Fig. 2, we systematically studied the etching effect by tuning the CH<sub>4</sub>/H<sub>2</sub> ratio. Fig. 2*a* shows an image of GNWs grown with the pure CH<sub>4</sub> flow, in which we could identify two kinds of structures, named stem (solid arrow) and branch (dashed arrow) structure, respectively. It is clear that the branch structure was much shorter and dimmer than the stem structure. However, when 5 sccm H<sub>2</sub> flow was added into the reaction, the branch structure disappeared, as shown in Fig. 2*b*. We attribute this phenomenon to the etching effect of hydrogen. According to the previous report, the preparation of GNWs was usually divided

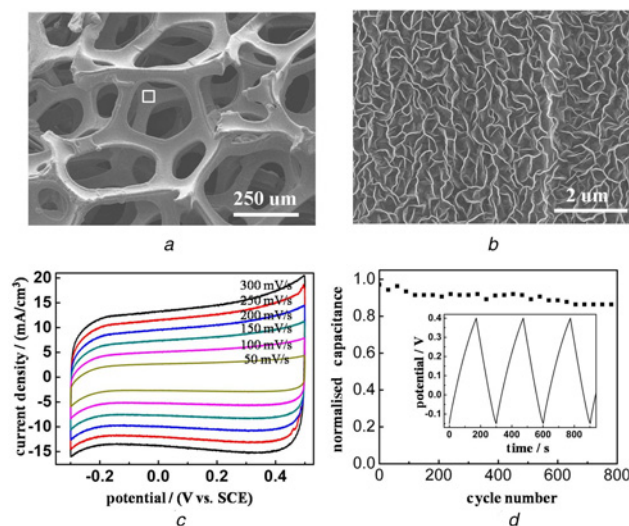


**Fig. 1** GNWs prepared on various substrates using PECVD method  
*a* Schematic illustration of the remote RF PECVD system  
*b* Photograph presents significant contrast between substrates before (left) and after (right) GNWs growth  
*c* SEM image shows the curled nanosheets structure of GNWs grown on copper foil. Growth parameter: 20 sccm  $\text{CH}_4$ , 5 sccm  $\text{H}_2$ , 600°C, 40 min  
*d* Raman spectrum of GNWs



**Fig. 2** Etching effect of hydrogen on the morphology of the GNWs. Growth parameter: 600°C, 40 min. All the scale bars are 500 nm. SEM images of GNWs grown on copper foil with a constant  $\text{CH}_4$  flow of 20 sccm and increase of  $\text{H}_2$  flow from  
*a* 0 sccm  
*b* 5 sccm  
*c* 10 sccm  
*d* 15 sccm

into two stages of nucleation and growth. These branch structures arose from the densely small nucleus formed at the nucleation stage. Nevertheless, when a high amount of hydrogen existed, the small nucleus could be easily etched away and only the growth of GNWs on the big nucleus survived. A few morphological changes occurred if we increased the  $\text{H}_2$  flow to 10 sccm (Fig. 2c). However, when the  $\text{H}_2$  flow was raised to 15 sccm, the formation of the big nucleus would also be suppressed due to the excessive etching effect, giving rise to the sparse GNWs as shown in Fig. 2d. Thus, an appropriate  $\text{CH}_4/\text{H}_2$  ratio was important for achieving the desired morphology.



**Fig. 3** Supercapacitor electrodes made of GNWs on nickel foam presented good electrical double-layer performance and cyclic stability

*a* Large-scale SEM image showing the skeleton of the nickel foam  
*b* Zoom-in SEM image showing the GNWs  
*c* CV curves of GNW electrode  
*d* Cyclic stability and galvanostatic charge/discharge (inset) measurements of GNW electrode. The current density used in the galvanostatic charge/discharge measurement was  $0.19 \text{ mA cm}^{-2}$

Supercapacitors are very attractive power storage devices for digital electronics and electric vehicles due to their several outstanding properties, such as high power density, high-rate charge/discharge performance and long cycle-life [15, 16]. However, the supercapacitor has a relatively smaller energy density than lead-acid and lithium-ion batteries, which obviously slow down its extensive use. There are two types of storage mechanisms for the supercapacitor: electrochemical double-layer capacitance (EDLC) and pseudocapacitance [17–19]. EDLC stores energy via charge accumulation at the electrode/electrolyte interface. Accordingly, the most practicable way to improve its energy density is increasing the accessible area of the electrode [20, 21]. The vertically standing nanosheets have an extremely high exposure area, moreover, the vacancies between the sheets of GNWs can facilitate the charge transfer at the interface, making the GNWs to be the promising candidates as the electrodes of the supercapacitor. Here we demonstrated that the GNWs grown on nickel foam showed good performance as the electrode.

The large-scale SEM image in Fig. 3a shows the skeleton of the nickel foam, and in the zoom-in image (Fig. 3b), the GNWs could be clearly identified. The growth parameter of GNWs was the same as that in Fig. 2b. It is worth noting that, in order to check whether the GNWs could be grown on the inner layer of the nickel skeleton, we intentionally zoomed into an inside area, as labelled by a small rectangle in Fig. 3a. The BET specific surface area of GNWs on nickel foam was  $25.1 \text{ m}^2 \text{ g}^{-1}$ , which was significantly larger than that of bare nickel foam ( $10.2 \text{ m}^2 \text{ g}^{-1}$ ). According to previous reports, the GNW film was hydrophobic, moreover, after oxygen-plasma treatment or chemical modification, the film would convert to be hydrophilic [22, 23]. A hydrophilic surface was crucial to increase the contact area at the electrode/electrolyte interface; hence, we pre-treated the GNWs using the oxygen-plasma method before electrochemical measurements. The oxygen plasma was triggered by 10 W RF for 1 min with an oxygen partial pressure around  $1 \times 10^3 \text{ Pa}$ . Fig. 3c presents the CV curves of the GNWs electrode recorded at various scan rates. The CV shape was nearly rectangular in the range of  $-0.3$  to  $0.5 \text{ V}$ , meaning a good electrical double-layer performance. The capacitances estimated from 50, 200, 300 mV/s were 0.053, 0.049,

0.047 F cm<sup>-3</sup>, showing a small 10% degradation at a high scan rate. Correspondingly, as shown in the inset image of Fig. 3d, the galvanostatic charge/discharge curves were nearly straight lines, further confirming that the GNWs worked well as EDLC. The specific capacitance calculated from the galvanostatic charge/discharge curve was 0.053 F cm<sup>-3</sup>. Moreover, the performance exhibited tiny degradation (<10%) after 800 charge/discharge cycles, as shown in Fig. 3d. As discussed in Fig. 2a, the GNWs showed plenty of branch structures without H<sub>2</sub> etching. Our measurements indicated that the supercapacitive performance was insensitive to the branch structures. Electrodes made of this kind of GNW presented good EDLC property and similar specific capacitance.

**4. Conclusion:** In conclusion, GNWs were prepared on a copper foil, nickel foam, and glass using the PECVD method. The etching effect of hydrogen played an important role in the growth of the GNWs. With lower hydrogen flow, a small nucleus could not be effectively eliminated, giving rise to abundant branch structures. In contrast, the higher hydrogen flow could etch away the big nucleus and presented the sparse-nanosheets morphology. Electrodes made of GNWs on nickel foam exhibited excellent electrical double-layer capacitance. Moreover, the high specific capacitance could be retained after hundreds of charge cycles, showing great potential in a future application.

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