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RAPID COMMUNICATION

Controllable preparation of vertically standing graphene sheets and their wettability and supercapacitive properties*

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Vertically standing graphene (VSG) sheets have been fabricated by using plasma enhanced chemical vapor deposition (PECVD) method. The lateral size of VSG nanosheets could be well controlled by varying the substrate temperature. The higher temperature usually gives rise to a smaller sheet size. The wettability of VSG films was tuned between hydrophobicity and hydrophilicity by means of oxygen and hydrogen plasma treatment. The supercapacitor electrode made of VSG sheets exhibited an ideal double-layer-capacitor feature and the specific capacitance reached a value up to 9.62 F·m^{-2}.

Keywords: vertically standing graphene, wettability, supercapacitor

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1. Introduction

Graphenes, two-dimensional crystals composed of densely packed sp^2 carbon atoms, have been extensively studied in recent years due to their unique physical properties and promising technological applications.[1–5] For single- or few-layer graphene, the orientation could be either horizontal or vertical, corresponding to the graphene sheets lying flat or standing vertically on the substrate, respectively. Recently, the VSG sheets have attracted enormous attention owing to their sharp-edge and high-surface-area characteristics. Previous studies have shown that the VSG film has many potential applications in field emission, solar cell and biotechnology.[6–9] Although lots of achievements have been made, some problems are still lack of elaboration. For example, VSG is synthesized mainly by plasma enhanced chemical vapor deposition (PECVD) technique, in which the substrate temperature is a key growth parameter. Though much effort has been made on the growth mechanism of VSG,[7,10] works engaged in studying the influence of substrate temperature on the growth of VSG sheets are rarely reported, which is obviously of great importance for fully understanding the growth mechanism.

In this paper, we systematically studied the influence of the substrate temperature on the lateral size of VSG sheets, and also discussed the possible growth mechanism. The contact angle (CA) for the VSG films were measured, and the wettability was manipulated between hydrophobicity and hydrophilicity through oxygen and hydrogen plasma treatment. Moreover, supercapacitor electrodes made of VSG sheets were fabricated and the electrochemical measurement was conducted.

2. Experimental section

2.1. Preparations of VSG sheets

The VSG film was fabricated in a PECVD system. The polycrystalline copper and nickel foils were cleaned by acetone and ethanol, and then were dried using argon gas. The Cu or Ni substrate was transferred to quartz tube furnace (reaction chamber). The furnace system was purged with 100 sccm (standard cubic centimeter per minute) H_2/Ar mixed gas (H_2, 10 vol%) and evacuated to a vacuum of 1×10^{-1} Pa. During the VSG film growth, the Cu or Ni substrate was heated to different temperatures (between 400 °C and 800 °C), then 20 sccm methane was inducted into the reaction chamber as the carbon source and simultaneously 120-W radio-frequency (RF) was generated to dissociate methane. At the end of the growth process, the plasma and methane gas were shut down, and then the system naturally cooled down to room temperature under the protection of 100-sccm H_2/Ar mixed gas.

2.2. Characterizations

The morphology of VSG sheets was observed using a field emission scanning electron microscope (FE-SEM, Hitachi S-4800) with an acceleration voltage of 10 kV. Raman spectroscopy was recorded using a Horiba Jobin Yvon LabRAM HR-800 Raman microscope with a laser wavelength of 532 nm and an incident power of approximately 1 mW.

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2.3. Contact angle measurements and O_2/H_2 plasma treatment of VSG samples

The CA measurement was conducted by a POWER-REACH contact angle measuring instrument using a 5-μL water droplet. In the oxidation and reduction experiments, the as-prepared VSG sample was loaded into the quartz tube furnace and the system was pumped down. The oxygen (hydrogen) plasma was generated by 10-W (30-W) radio frequency with an oxygen (hydrogen) partial pressure kept at 6 Torr (6 Torr).

2.4. Electrochemical measurements

The cyclic voltammetry (CV) and galvanostatic charge/discharge (CC) measurements were carried out on CHI 660D electrochemical workstation using a three-electrode system. A saturated calomel electrode (SCE) and a platinum wire were used as the reference electrode and the counter electrode, respectively. The electrolyte was 1M NaAc and 1M $MgSO_4$ mixed solution. All of the measurements were performed at room temperature.

3. Results and discussion

3.1. Controllable preparation of VSG sheets

The RF in PECVD system can dissociate methane into various active species, such as CH_x, atomic C and H. Adsorption and nucleation of these radicals give rise to the formation of VSG.[8] Because the carbon feeding does not only rely on the catalytic decomposition by the substrate, the VSG film can be prepared on almost arbitrary substrates, such as copper, nickel, silicon and glass.[8,11] Figures 1(a) and 1(b) show the typical SEM images of VSG grown on copper foil at 600 °C. It can be seen that large-area and uniformly distributed VSG was formed on copper substrate and exhibited a sheet-like structure with open edges. The cross-sectional SEM image demonstrates that the graphene sheets were vertically standing on the copper substrate with a height of 390 nm, as shown in Fig. 1(c). In the Raman spectrum (Fig. 1(d)), three peaks locating at 1350 cm^{-1}, 1581 cm^{-1}, and 2693 cm^{-1} can be clearly identified, corresponding to D peak, G peak and 2D peak, respectively. The high-intensity of D peak is mainly due to the existence of the massive edge carbons. The G and 2D peaks were associated with the doubly degenerate zone center E_{2g} mode and the secondorder of zone-boundary phonons, having the full width at half-maximum (FWHM) of 32 cm^{-1} and 54 cm^{-1}, respectively.[7] The intensity ratio of the 2D peak to the G peak (I_{2D}/I_G) represents the number of layers of the sheets.[12,13] In the spectrum, the 2D band ratio I_{2D}/I_G is about 1. Thus, the as-prepared VSG sheets have about 5–8 layers.[12]

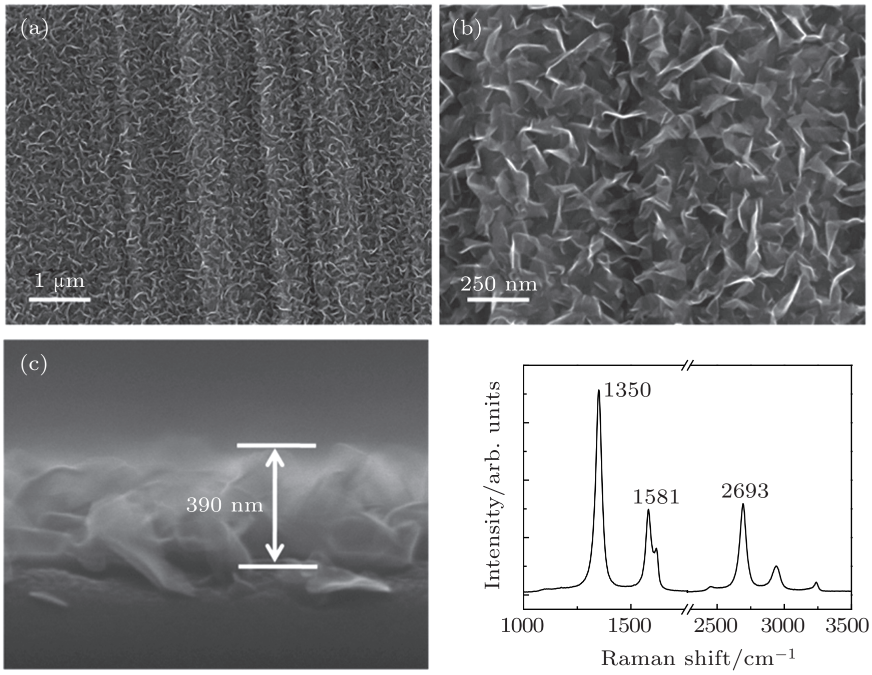

Fig. 1. A large-scale SEM image (a) and a zoom-in image (b) of VSG grown on copper foil. VSG shows a sheet-like structure. (c) Cross-sectional SEM image of VSG. (d) Raman spectroscopy of VSG.

The influence of substrate temperature on the growth behavior was investigated. We found that the higher growth temperature usually gave rise to a smaller sheet size. As shown in Fig. 2, the sheet sizes of VSG prepared with the substrate temperatures of 700 °C, 600 °C, and 500 °C were about 50 nm, 150 nm, and 350 nm, respectively. According to previous study, the growth process of VSG was composed of two stages: firstly, the carbon precursors nucleated and the growth followed a layer-growth mode, forming massive graphene islands parallel to the substrate surface; secondly, due to the accumulation of strain energy, two-dimensional growth was no longer energetically favorable, therefore the leading edge at the island boundaries curled upwards and subsequently a vertical growth mode started.[7,10] Moreover, Zhang *et al.* reported that at the first growth stage, more nucleation sites would be created at the higher substrate temperature, leading to relatively smaller size of islands.[14,15] By summarizing above discussion we could explicitly interpret the phenomenon observed in our experiment (Fig. 2(d)): with the rising temperature, islands with smaller sizes were inclined to form; smaller islands had shorter circumferences, once the transition to the vertical growth was triggered around the boundaries, VSG with smaller sheet size took shape. This result provides further strong evidence for the two-stage growth mechanism.

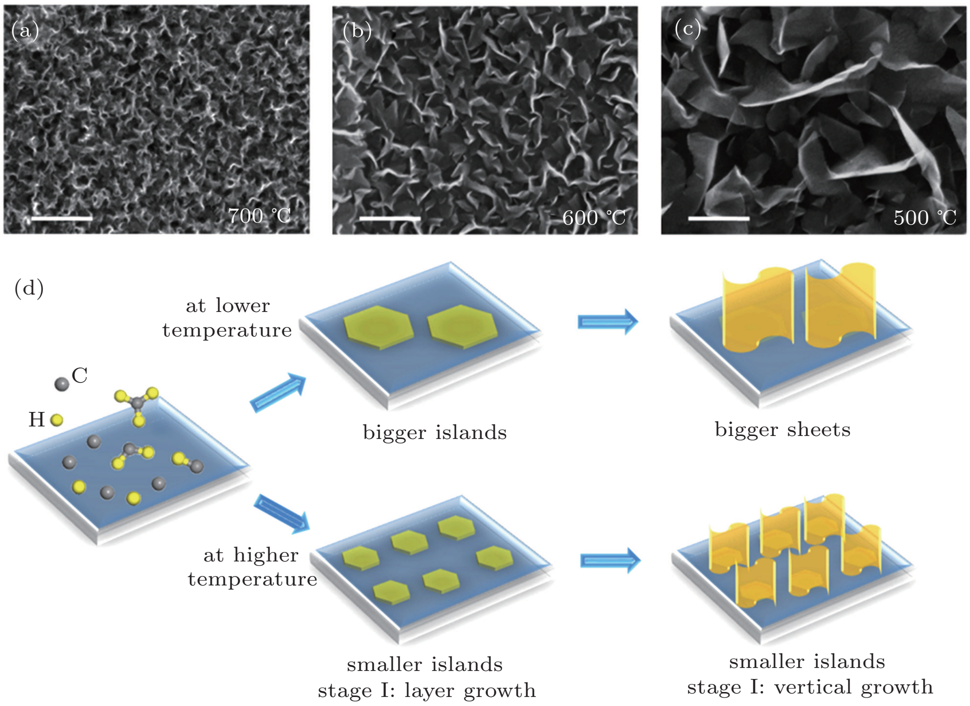

Fig. 2. (color online) (a), (b), and (c) SEM images of VSG prepared at different substrate temperatures. Higher temperature gave rise to a smaller lateral size of the VSG sheets. All the scale bars are 200 nm. (d) Schematic diagram of the two-stage growth mechanism of VSG.

3.2. Tuning the wetting property of VSG film

Hydrophobic and hydrophilic surfaces are extensively used as anti-contamination and water-proofing films in coating, optoelectronics, and biochemical devices.[16–18] Therefore, the wettability of graphene has been widely investigated since its discovery in 2004.[11,19,20] According to previous study, the manipulation of the wettability of graphene between hydrophobic and hydrophilic was realized mainly through chemical modified method. Wong *et al.* increased the CA of graphene oxide (GO) film from 67.4° to 132.4° by functionalizing GO with octadeylamine (ODA).[19] Dong *et al.* reported that the oxidation treatment could change the CA of VSG grown on silicon from 132.9° to 53.1°, moreover, the value recovered to 133.7° by further ODA treatment.[11] However, these chemical procedures are complicated and time-consuming, herein we present a facile way to tune the wettability of VSG by treating the surface with oxygen and hydrogen plasma.

The VSG film grown on copper foil at 600 °C was used to conduct the CA measurement. It is worth mentioning that, as discussed above, VSG films with different sheet sizes could be prepared by varying the growth temperature, however, we did not find an obvious dependence of CA on the sheet size in our wetting experiment. Figure 3(a) shows a typical image of water droplet on the untreated VSG film. The CA was 140.1°, indicating that the VSG film is a hydrophobic surface. It can be interpreted that the CA of pure graphene is around 95°, but the rough and sheet-like structures of VSG film have the capability to enhance the hydrophobicity.[20,21] The wettability underwent a significant transition to hydrophilicity with a CA of 0° after oxygen plasma treatment for 35 s, as shown in Fig. 3(b). This phenomenon was attributed to that many hydrophilic functionalities such as carbonyls and epoxide groups were added onto the surface of VSG during the oxidation procedure.[22,23] In addition, these oxygen-containing groups could be eliminated by further hydrogen plasma treatment for 2 min and the VSG film recovered its hydrophobic surface with a CA of 133.0° (see Fig. 3(c)). Figure 3(d) shows a plan view SEM image after oxidation procedure, from which we could clearly indentify the well-preserved sheet structure, indicating the VSG film was not damaged during the plasma treatment. These results demonstrate that the wettability of VSG has been tuned by utilizing the plasma approach. It is facile to handle compared with chemical modification method.

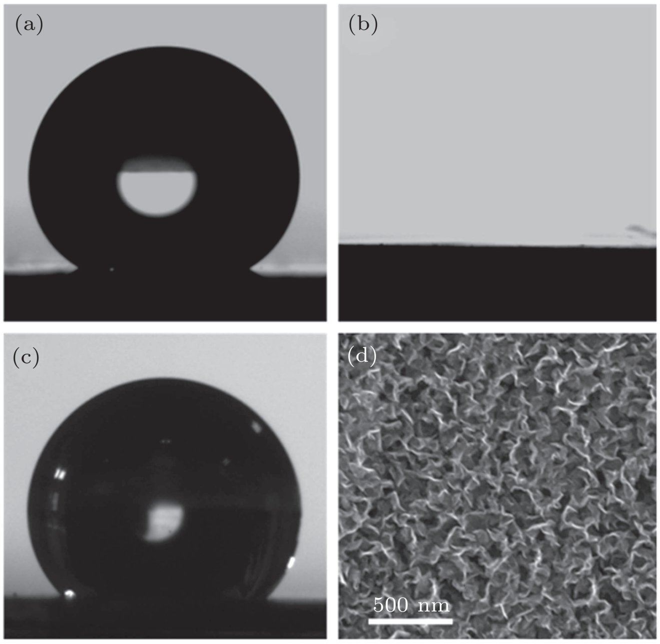

Fig. 3. (a) Pristine VSG is hydrophobic with a CA of 140.1°. (b) After O_2-plasma treatment, VSG converts to be hydrophilic with a CA of 0°. (c) After subsequently H_2-plasma treatment, VSG recovers to be hydrophobic with a CA of 133.0°. (d) SEM image of VSG after oxidation treatment. The well preserved sheet structure indicates that VSG has not been damaged during the plasma treatment.

3.3. Supercapacitor behaviors of VSG film

Supercapacitors are very promising power sources in many applications owing to their higher charge/discharge rate and longer cycle-life compared with batteries.[5,24] There are two types of supercapacitors: electrochemical double-layer capacitors (EDLCs) in which the energy-storage uses ion adsorption, and pseudocapacitors using fast surface redox reaction.[25] Carbon-based materials have been extensively studied as electrodes in EDLCs due to their unique integrations of properties such as lightweight, high electrical conductivity and electrochemical stability.[26–28] As the energy-storage of EDLCs mainly depends on the electrostatic interaction between high-surface-area electrodes and electrolyte ions, control of the structure and morphology of carbon materials to enlarge their exposure area in electrolyte is crucial to improve the capacitor's performance.[26,27] Much effort has been made following this strategy. Yoo *et al.* reported that the "in-plane" design in capacitor allowed for more efficiently utilization of graphene surface area than the "stacked" design, and a specific capacity up to 3.94 $F\cdot m^{-2}$ was observed.[26] Liu *et al.* demonstrated that the curved sheet morphology was capable of preventing graphene sheets from face-to-face restacking and made it possible to fully utilize the electrode surface area.[27]

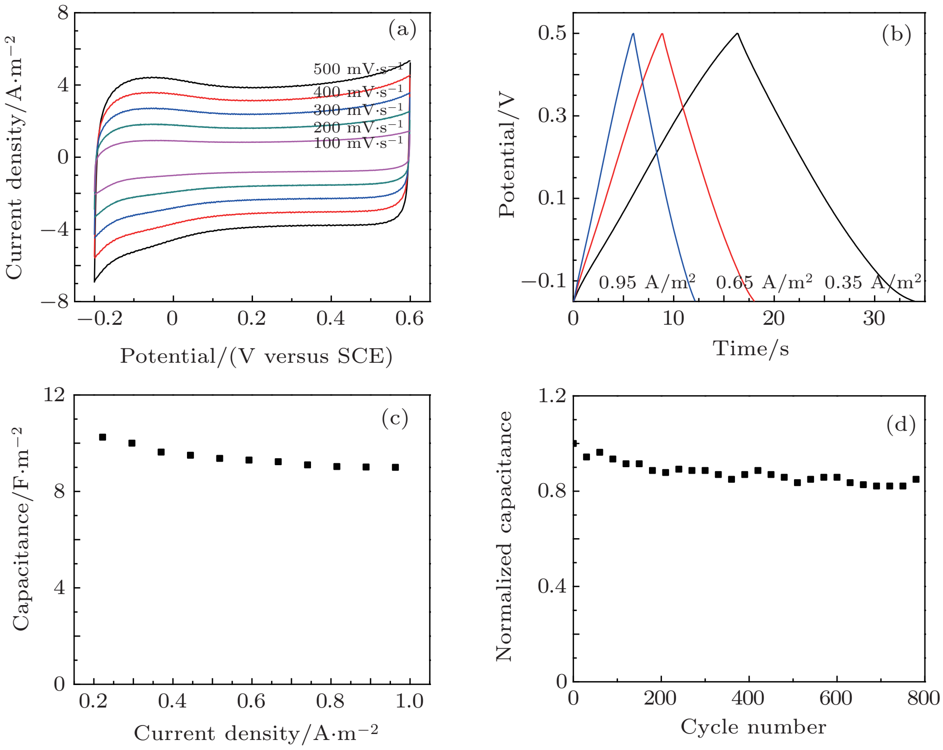

Fig. 4. (color online) The cyclic voltammetry (a) and galvanostatic charge/discharge (b) measurements of the electrode made of VSG. (c) The specific capacitance recorded at different current densities. (d) Cyclic stability measurement of the VSG-based capacitor.

The VSG film grown on a nickel foil was used as the working electrode. The nickel foil acted directly as the current collector, thus the complicated transfer and coating procedures to other collectors were circumvented. Figure 4(a) shows CV curves of VSG electrode recorded at different scan rates. These curves exhibit an approximately rectangular shape in the range of −0.2 V–0.6 V, which is the key feature of ideal double-layer capacitors. Correspondingly, the CC curves recorded at different current densities in Fig. 4(b) also exhibit a symmetric triangular shape, further confirming the establishment of an efficient electrical double-layer. Specifically, at a current density of 0.35 A·m^{-2}, the VSG film shows a specific capacitance of 9.62 F·m^{-2}, much higher compared with 2.79 F·m^{-2} and 3.94 F·m^{-2} reported previously.[26,29] To elaborate the advantages of the VSG film, a controlled experiment was carried out by preparing graphene in the form of planar layers flat lying on the nickel surface. The electrode made of the flat-lying graphene presents a capacitance of 0.06 F·m^{-2}, which is about two orders of magnitude lower than that of VSG film. This result implies that the sheet-standing structure of VSG film significantly enlarges the accessible surface area, enabling more effective ion transport and adsorption. Moreover, the VSG electrode maintains a high specific capacitance in a wide range of current densities, showing a capacitance of 9.03 F·m^{-2} at the high current density of 0.95 A·m^{-2} (Fig. 4(c)). Additionally, as shown in Fig. 4(d), the film retains 85% of its initial capacitance after 800 charge–discharge cycles, presenting great potential for future applications.

4. Conclusion and perspectives

In conclusion, VSG was prepared by using the PECVD method. We found that the substrate temperature had a significant influence on the lateral size of VSG nanosheets. Higher growth temperature would give rise to a smaller sheet size. The pristine VSG film was a hydrophobic surface with a CA of 140.1°. The wettability could be converted to hydrophilicity after oxygen plasma treatment with a CA of 0°. Additionally, the oxidized VSG film could recover to a hydrophobic surface by further reduction with hydrogen plasma. The supercapacitor electrode made of VSG exhibited excellent performance with a specific capacitance as high as 9.62 F·m^{-2}. The capacitor was able to maintain its high capacitance at a wide range of current densities and after long-term charge/discharge tests. Our results are helpful in understanding the growth mechanism of VSG sheets and exploring their potential applications.

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