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# Catalyst-free approach for growth of graphene sheets on high-density silica nanowires by CVD



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## ABSTRACT

A novel “two-step annealing” method is proposed for the direct synthesis of graphene sheets on high-density dielectric silica nanowires without using metal catalysts. During the first annealing at 1000 °C, the extremely thin SiO<sub>2</sub> layer on Si substrate shrinks and forms dense nanoparticles. Using these silica nanoparticles as templates, graphene sheets and silica nanowires are synthesized simultaneously after the second annealing process at 800–850 °C. The experiment results suggest that the graphene sheets grow along the nanowires and its crystalline quality and domain size are determined by the temperature and duration of the second annealing process.

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## 1. Introduction

Graphene, a fascinating monolayer or few layers film of sp<sup>2</sup> bonded carbon atoms [1], has attracted much attention due to the unique properties such as high carrier mobility, mechanical/chemical stability, tunable energy band structure and acceptable optical transparency [2–6]. Since the discovery of graphene in 2004, there has been extensive research on the synthesis of graphene. Among the proposed techniques, the growth of graphene by chemical vapor deposition (CVD) on metal catalysts or semiconductor catalysts [7] has been considered as the most promising technique because of the simple process and the capability of achieving large area graphene with high crystalline quality. However, chemical etching and transfer with a polymer support layer may inevitably introduce defects, impurities, wrinkles, and cracks, thus potentially degrading the performance of graphene-based devices. To bypass the wet chemical processing, the synthesis of graphene on dielectric substrates with catalyst-free process has been recently suggested [8]. Herein, we propose a cost-efficient and catalyst-free “two-step annealing” method to grow high quality graphene sheets on silica nanowires directly. This graphene/silica nanowires material has been considered as a promising anode material for lithium-ion batteries [9] and can be

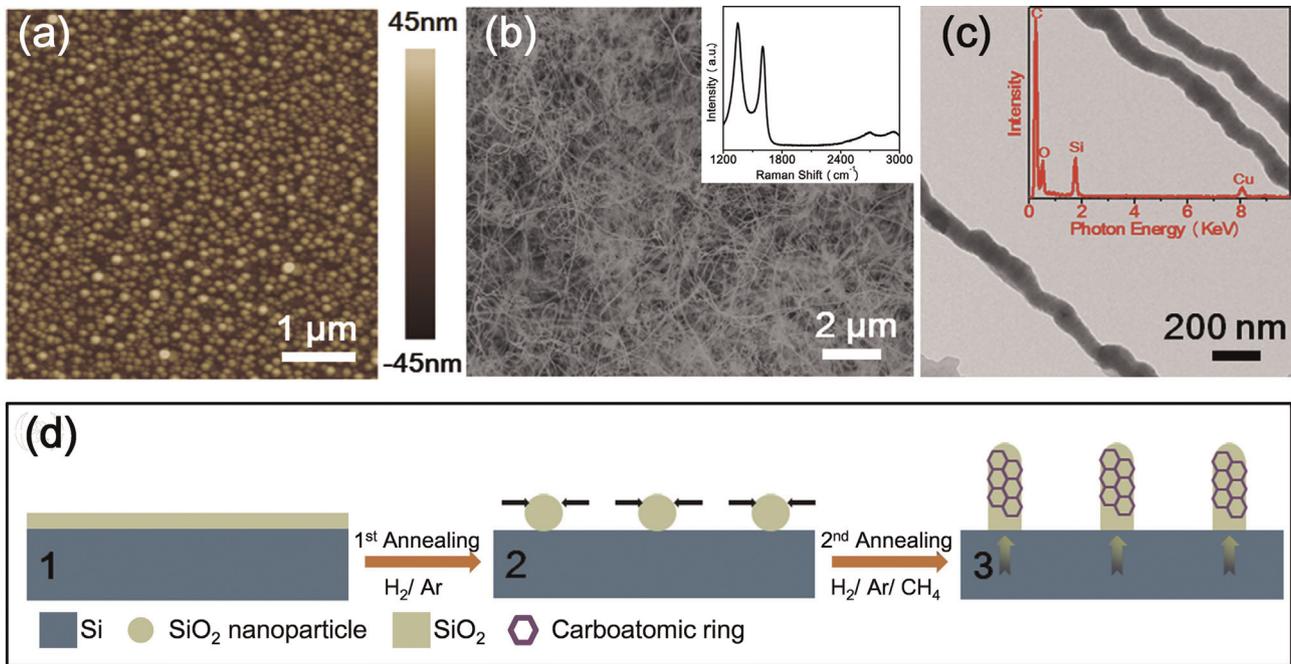
readily applied to the fabrication of nanoscale electrode [10]. In addition, the graphene sheets on silica nanowires could be transferred easily to other substrate by ultrasonic-dispersion method for some applications such as thin-film resistors, transparent conductive films, and floating gate memory [8,11].

## 2. Experiments

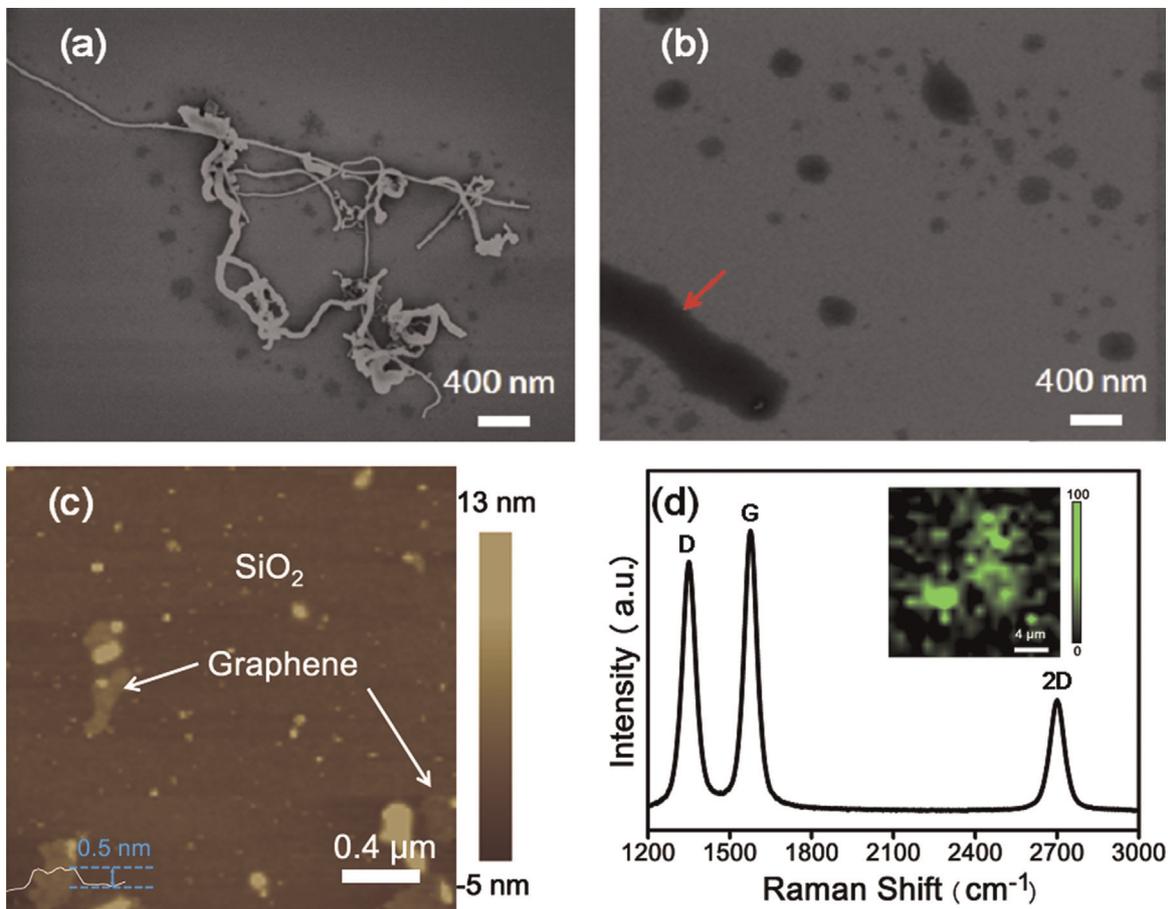
The synthesis of silica nanowires and graphene sheets was carried out in an atmospheric pressure chemical vapor deposition (APCVD) system. Si substrates with a 7 nm-thick thermal oxide layer were firstly pretreated by sonication in acetone, ethanol and deionized (DI) water for 10 min successively. Then the samples were placed in the center of quartz glass tubular reactor, heated to 1000 °C and annealed for 150 min to form silica nanoparticles under a flow of Ar (200 sccm)/H<sub>2</sub> (20 sccm). As the system temperature dropped from 1000 °C to the target of 750–850 °C with a low rate (10 °C/min), the samples were annealed again for 50–150 min for the growth of silica nanowires and graphene sheets under a flow of Ar (200 sccm)/H<sub>2</sub> (20 sccm)/CH<sub>4</sub> (0.45 sccm). During the whole process, the pressure in the tubular reactor was maintained as atmospheric pressure.

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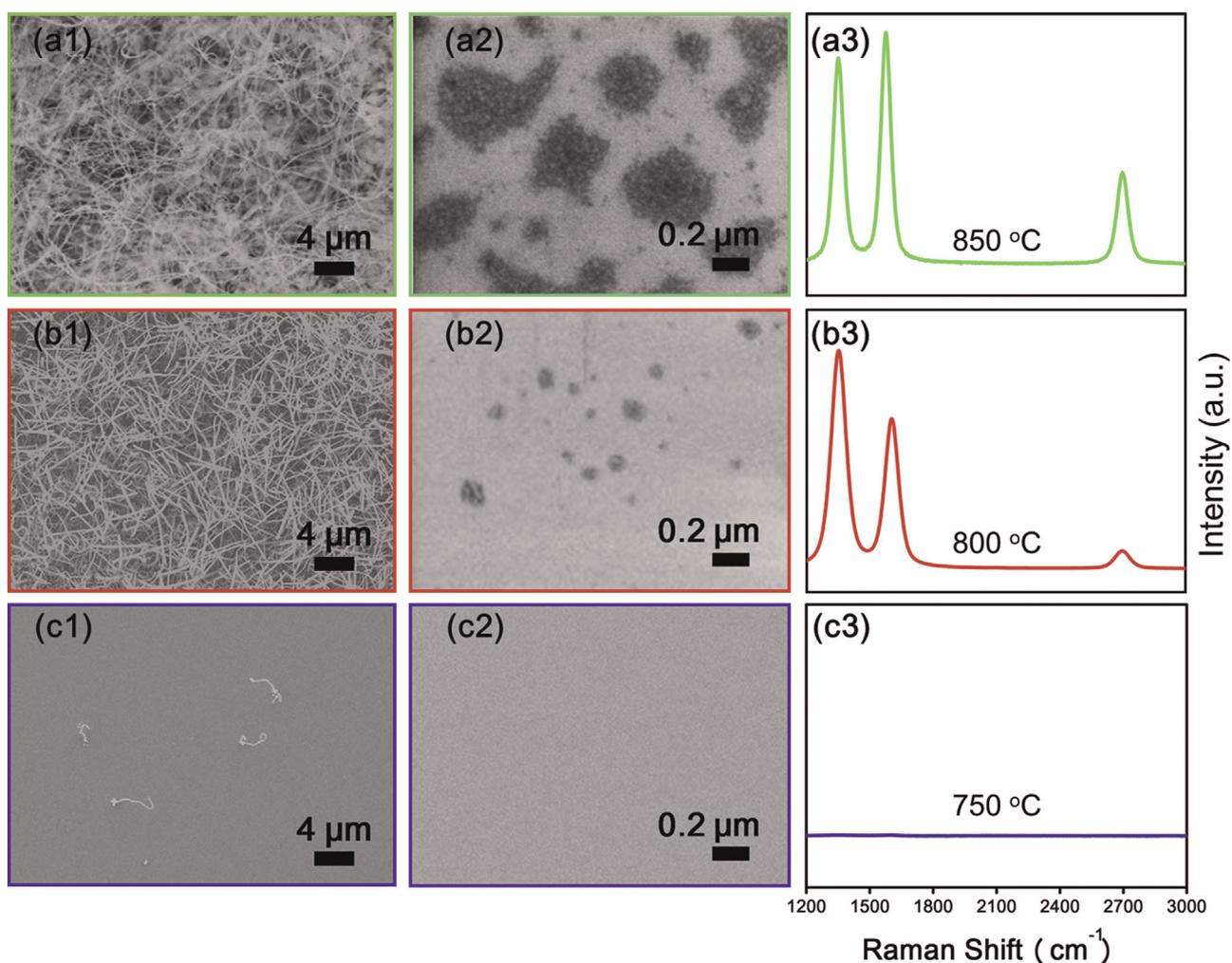
E-mail address: [simsnow@mail.sim.ac.cn](mailto:simsnow@mail.sim.ac.cn) (Z. Xue).



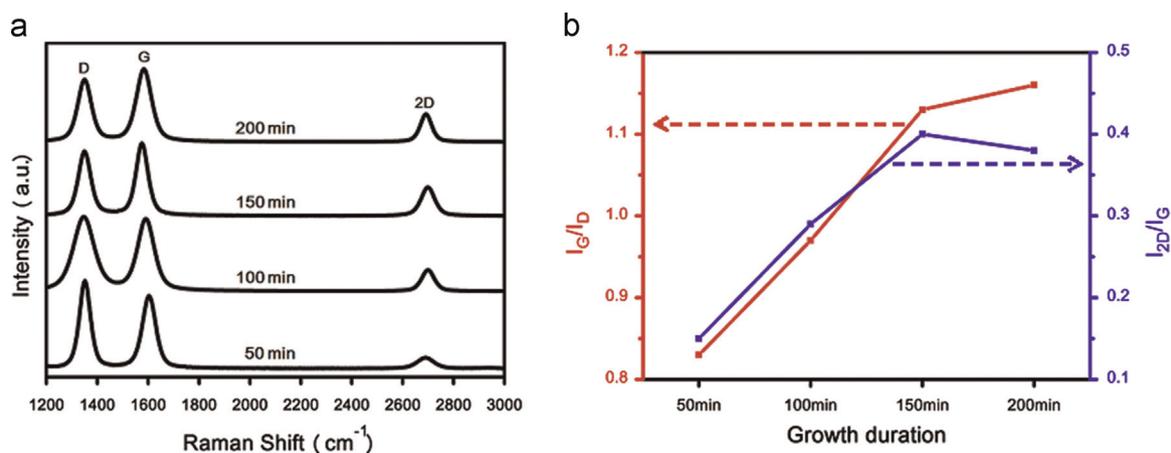
**Fig. 1.** Process flow of the synthesis of SiO<sub>2</sub> nanowires and graphene sheets. (a) Tapping-mode AFM image of SiO<sub>2</sub> nanoparticles formed at 1000 °C. (b) SEM image of graphene/SiO<sub>2</sub> nanowires formed at 850 °C. The inset is the corresponding Raman spectrum. (c) TEM image of graphene sheets on SiO<sub>2</sub> nanowires. The inset is the EDS of individual nanowires. (d) Schematic illustrate of the growth mechanism: (1) initial sample; (2) annealed at 1000 °C; (3) annealed at 750–850 °C.



**Fig. 2.** Characterization of graphene sheets transferred to 300 nm SiO<sub>2</sub>/Si substrates. (a) and (b) SEM images of typical graphene sheets; (c) the AFM image of the transferred graphene sheets; (d) the Raman spectrum and Raman 2D-mapping of graphene sheets. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)



**Fig. 3.** SiO<sub>2</sub> nanowires and graphene sheets grown at different temperatures. (a1), (b1) and (c1) show pristine samples synthesized at 850 °C, 800 °C, 750 °C, respectively. (a2), (b2) and (c2) are the SEM images of graphene sheets transferred to SiO<sub>2</sub>/Si substrates. The corresponding Raman spectra are shown in (a3), (b3) and (c3).



**Fig. 4.** (a) Raman spectrum of graphene sheets synthesized under optimal temperature for different durations. (b) I<sub>G</sub>/I<sub>D</sub> and I<sub>2D</sub>/I<sub>G</sub> ratios versus the growth durations.

### 3. Results and discussion

Fig. 1 shows the process of catalyst-free “two-step annealing” for the synthesis of graphene sheets on high-density silica nanowires. The tapping-mode atomic force microscopy (AFM) image (Fig. 1(a)) was used to characterize the samples’ surface morphology after the first annealing process at 1000 °C for 150 min. It can be found that intensive silica nanoparticles were formed. As

the obtained silica nanoparticles was treated by the second annealing process under a flow of Ar/H<sub>2</sub>/CH<sub>4</sub> at 800–850 °C for 50–150 min, high-density nanowires with a typical length up to a few hundred micrometers and diameters in the range of 20–200 nm were formed on the sample surface (Fig. 1(b)). The inset Raman spectrum of Fig. 1(b) indicates that graphene sheets were synthesized accompanied by the formation of nanowires. The transmission electron microscopy (TEM) image (Fig. 1(c)) shows that

there are some small fragments stuck on nanowire surface. The energy dispersive X-ray spectroscopy (EDS) analysis indicates that the nanowires and the fragments are mainly composed of C, Si and O elements. Based on the Raman, TEM and EDS results, it can be deduced that those small fragments observed by TEM correspond to graphene sheets. These procedures can be demonstrated using a schematic (Fig. 1(d)). As shown by step 2, the 7 nm-thick thermal oxide layers could shrink and form nanoparticles due to surface tension under high temperature. Then Si atoms diffused from the substrate to the nanoparticles, and reacted with O atom to form nanowires [12]. The oxygen might come from the source materials ( $\text{SiO}_2$ ) or from the residue  $\text{O}_2$  gas in the chamber and carrier gas [13]. Meanwhile, the carbon atom from methane is fairly easy to deposit on the silica nanowires surface to form graphene sheets due to the curved surface [14].

The synthesized graphene sheets were transferred onto a 300 nm  $\text{SiO}_2/\text{Si}$  substrate by dispersion-ultrasonic method for the further characterization by scanning electron microscopy (SEM), AFM and Raman microscope. As shown by Fig. 2(a), all the graphene sheets distribute around nanowires and the sizes of graphene sheets are comparable to the widths of the nanowires, which suggests that the graphene sheets peel off from the nanowires. The graphene sheet indicated by red arrow in Fig. 2 (b) shows the graphene sheets may grow on the nanowire in the conformal manner. Tapping mode AFM image (Fig. 2(c)) indicates the thickness of graphene sheets is approximately 0.5 nm, which corresponds to a single graphene layer. Fig. 2(d) shows a typical Raman spectrum of transferred graphene sheets: the position and FWHM of 2D peak, along with  $I_{2D}/I_G$ , indicate that graphene mainly consists of  $\text{sp}^2$  graphitic bonded carbon [15]. The uniformity of graphene sheets was exhibited by the color-coded intensity mapping of the 2D peak (inset of Fig. 2(d)), which was measured with a spot size of 1  $\mu\text{m}$  and step size of 1  $\mu\text{m}$ . The green regions correspond to graphene sheets and the dark regions represent the  $\text{SiO}_2$  surface. The intensity mapping manifests that many graphene sheets were transferred onto the  $\text{SiO}_2/\text{Si}$  substrate and every single graphene sheet possesses high uniformity.

The dependence of crystalline quality and domain size of graphene sheets on the growth temperature was studied in this work. Fig. 3(a1), (b1) and (c1) shows the SEM images of pristine samples grown at 850, 800 and 750  $^\circ\text{C}$ , respectively. Fig. 3(a2), (b2) and (c2) shows the SEM images of transferred graphenes. Fig. 3(a3), (b3) and (c3) shows the corresponding Raman spectra of transferred graphene sheets. At 750  $^\circ\text{C}$ , there are extremely sparse silica nanowires with lengths of about 5  $\mu\text{m}$  on the sample surface (Fig. 3 (c1)), and no graphene sheets are observed from Fig. 3(c2). The corresponding Raman spectrum (Fig. 3(c3)) also evidences the lack of graphene sheets. At 800  $^\circ\text{C}$ , high-density silica nanowires with diameters ranging from 20 to 200 nm and lengths of ten micrometers were grown and distributed over the entire area of the substrate (Fig. 3(b1)). Correspondingly, a very small amount of graphene sheets with domain size ranging from 10 nm to 160 nm were obtained (Fig. 3(b2)). For these graphene sheets, although the typical Raman features of graphene, i.e., the 2D peak and the G peak, appear, the large defect related D peak with a peak intensity ratio of  $I_D/I_G \approx 1.7$  demonstrates the presence of strong defects and edge effect in graphene sheets. At 850  $^\circ\text{C}$ , the lengths and diameters of high-density silica nanowires reach to a few hundred micrometers and a few hundred nanometers, respectively (Fig. 3 (a1)). Meanwhile, the domain size of graphene sheets increases up to a few hundred nanometers (Fig. 3(a2)). As compared in Fig. 3 (b3) and (a3), the attenuation of the D peak and the significant

reduction of peak intensity ratios  $I_D/I_G$  from 1.7 to 0.9 indicate the crystalline quality of graphene sheets is improved as the growth temperature increases from 800  $^\circ\text{C}$  to 850  $^\circ\text{C}$ .

Fig. 4 shows the Raman spectra and peak intensity ratios of graphene sheets grown at optimal temperature (850  $^\circ\text{C}$ ) for various durations. During the growth period of 50~150 min, the defect-related D peak recedes gradually, while the intensity of  $\text{sp}^2$ -related 2D peak increases and its FWHM value decreases as the growth proceeds. Besides that, the peak intensity ratios  $I_G/I_D$  and  $I_{2D}/I_G$  rise from 0.83 to 1.13 and from 0.15 to 0.4, respectively. Therefore, it is concluded that the quality and domain size of graphene sheets improves gradually during these growth periods. However, the evolution of graphene sheets including the crystalline quality and domain size is ceased as the growth process extends from 150 to 200 min as evidenced by the barely changed Raman, which implies that the graphene domain size may be restricted to the transverse size of silica nanowires.

#### 4. Conclusions

In conclusion, we have developed a facile two-step annealing process to grow high-quality graphene sheets directly on high-density silica nanowires by APCVD without using metal catalysts. By annealing a 7 nm  $\text{SiO}_2/\text{Si}$  sample at 1000  $^\circ\text{C}$ , dense silica nanoparticles were formed on the sample surface. Using these silica nanoparticles as templates, graphene sheets and silica nanowires were synthesized simultaneously during the second annealing process at 800–850  $^\circ\text{C}$ . Parametric studies show that the crystalline quality and domain size of graphene sheets depend on the temperature and duration of second annealing step. This method may pave a new way for catalyst-free growth of graphene sheets with low cost.

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