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Crystallographic Tailoring of Graphene by Nonmetal SiO_x Nanoparticles

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Due to high electron mobility and long coherence length, graphene has attracted increasing interest as a promising new material for next-generation electronics. However, a major problem for mainstream logic applications is that graphene remains metallic even at the neutrality point.[1] The construction of atomically precise graphene nanoribbons (GNRs) is considered to be an ideal way to open a gap in the electronic structure of graphene. Theoretical studies predicted that this gap depends on the width and crystallographic orientation of GNRs.[2] In addition, nanosized triangular and hexagonal graphene pieces terminated by zigzag edges are predicted to have unique magnetic properties.[3] Therefore, tailoring graphene into GNRs or regular pieces with desired structures is highly required for device applications. In addition to e-beam lithography,[4] scanning tunneling microscope lithography,[5] and chemical stripping,[6] catalytic tailoring by metal nanoparticles (NPs) of Fe,[7] Ni,[8] and Ag[9] has been recently developed to tailor graphene into GNRs, which has great potential for atomically precise graphene device fabrication with controllable crystallographic orientation.

However, metal NPs remaining in the tailored graphene influence the intrinsic properties[10] of graphene. Especially, most residual metals are not compatible to and highly prohibited in complementary metal-oxide semiconductor (CMOS) processes,[11] which limits the tailored GNRs or nanosized pieces by metal NPs for device applications. Moreover, the tailoring directions can vary depending on the specific catalyst used because of the different interactions between NPs and graphene edges.[7−9] Therefore, exploring new catalysts is important for the controlled tailoring of graphene. Additionally, the catalytic hydrogenation mechanism has been proposed for the tailoring of graphite by Fe[12] and Ni[13] NPs, similar to that occurring in the methanation reaction and hydrocarbon production from coal. However, nonmetals are rarely reported to exhibit catalytic activity for the hydrogenation of carbon materials, so graphene is considered not to be tailored by nonmetals. In this communication, we report that nonmetal SiO_x NPs can be used to tailor graphene into GNRs or regular pieces with smooth edges and preferential crystallographic orientation. These findings indicate the potential catalytic activity of SiO_x NPs for the hydrogenation of carbon materials, and this technique opens up the possibility for atomically precise graphene device fabrication without metal contamination.

Few-layer graphenes (FLGs) were prepared and transferred onto the substrates of a Si wafer capped with 280 nm of SiO_2 by micromechanical rubbing (for details, see Supporting Information, SI).[14] We used an optical microscope to locate the samples.[15] Atomic force microscope (AFM) and scanning electron microscope (SEM) measurements indicate that there are no trenches and NPs for the as-prepared FLGs. Then the sample was transferred to a furnace and annealed in a H_2 flow (40 sccm) at 850−1100 °C (no tailoring occurs at less than 850 °C). During this annealing process, many NPs of mostly less than 30 nm in diameter were formed from the Si/SiO_2 substrate and deposited beside the edges of FLGs or onto them (Figure 1a), which initiates the tailoring processes of FLGs. The tailoring results of FLGs were detected by AFM and SEM.

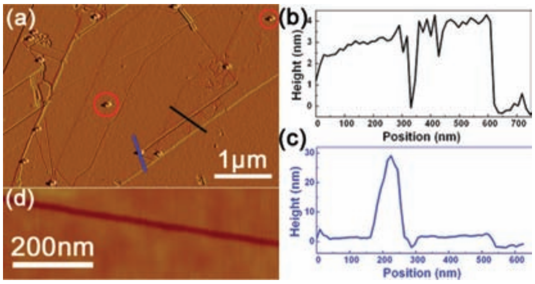

Figure 1. FLGs tailored by SiO_x NPs. (a) AFM image of FLGs, annealed for 10 min. (b) Height profile along the black line in (a), showing the depth of trenches can be down to the substrate. (c) Height profile along the blue line in (a), showing the size of NPs used for the tailoring of FLGs. (d) AFM image of a trench, showing that its width is less than 30 nm.

Figure 1a shows the AFM image of an FLG after the tailoring procedure. Many straight trenches are observed in the FLG along which carbon atoms have been removed. Detailed AFM height analysis (Figure 1b) shows that the majority of these trenches are etched down to the substrate, and the width of trenches is usually smaller than 30 nm. High resolution AFM (the radius of AFM tip is smaller than 2 nm) measurements reveal that the trench edges are smooth within the probe limit, as shown in Figure 1d. Moreover, it is worth noting that the angles between different trenches are 30°, 60°, or 120°, which indicates that the tailoring follows crystallographic orientations of the graphene honeycomb lattice. High resolution X-ray photoelectron spectroscopy (XPS) analyses indicate that the tailored FLGs contain only Si, O, and C and no metal species such as Fe, Co, Ni, and Cu (see SI), which suggests that the NPs for the tailoring of FLGs are nonmetal.

To demonstrate the formation and elucidate the nature of these NPs, we placed a piece of highly oriented pyrolytic graphite (HOPG) downstream from the Si/SiO_2 wafer (Figure 2a), and there are no NPs and trenches on the surface of the original HOPG (see SI). After annealing at 900 °C in H_2, many trenches and NPs of different sizes are formed on the surface of the HOPG (Figure 2b and 2c). XPS measurements reveal that Si and O signals appear after annealing compared to the case of the original HOPG (see SI). High resolution XPS of the *in situ* formed NPs shows a peak at 102.1 eV, which is similar to the bonding energy of the Si/SiO_2 surface (102.2 eV). The Si compounds of O or C show obviously different XPS features, where Si in SiO_x is at 100.4−104.0 eV, Si in SiC is at 99.8−100.8 eV, and pure Si is at 98.7−99.6 eV.[16] In combination with the presence of the O signal in the same sample, the peak at 102.1 eV observed for the *in situ* formed NPs is assigned to Si in SiO_x. The above results suggest that the SiO_x NPs are

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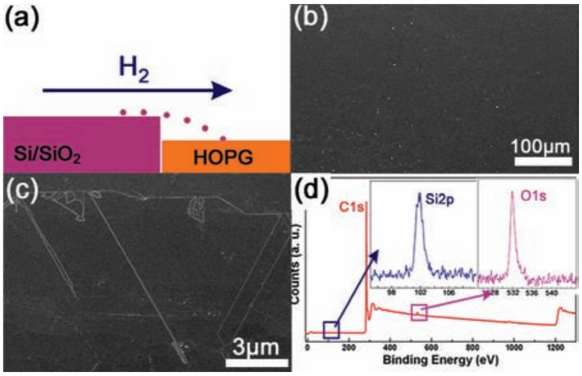

Figure 2. Formation of SiO_x NPs. (a) Schematic of the formation of SiO_x NPs from Si/SiO_2 substrate and flow to HOPG. (b, c) SEM images of the HOPG surface after annealing, showing many NPs and tailored trenches on it. (d) High resolution XPS result of HOPG after annealing, showing the formed NPs should be SiO_x species.

formed from the Si/SiO_2 wafer at elevated temperature and tailor the HOPG in a H_2 atmosphere.

Systematic experiments reveal that the presence of SiO_x NPs and H_2 is crucial for the tailoring of FLGs. No trenches are obtained without the assistance of NPs even in a H_2 atmosphere, which can be confirmed through the annealing of HOPG. Moreover, the trench width strongly depends on the size of NPs. Generally, wider trenches can be obtained for big NPs than small NPs. On the other hand, the FLGs are randomly etched from the edges in an Ar atmosphere regardless of whether there exist NPs or not as occurs in Ar/O_2 atmosphere.[17] Moreover, we find that the tailoring results seem to be irrelevant to the flow rate of hydrogen. In contrast to the etching in an oxygen atmosphere,[17] no thickness dependent tailoring was found for the SiO_x NPs in a H_2 atmosphere. Evidence of this is found in the fact that, for the same NP, the tailoring direction does not change when the thickness of the tailored graphene layers is changed (all details, see SI).

To elucidate the tailoring process, we investigated the trench evolution with annealing time (Figure 3), and some useful information for the tailoring of FLGs by SiO_x NPs is found: (i) All the trenches can be traced to the edges of FLGs, and there is always an NP at the end of the trench. This suggests that the tailoring starts from the reaction of NPs and carbon atoms at the edges, since these atoms are more active than those within the graphene sheet. This can be further confirmed by the fact that no tailoring occurs for the deposited NPs within the sheet, as indicated by the circles in Figure 1a. (ii) The tailoring of FLGs proceeds with the movement of NPs, and the tailoring direction changes when the NP meets the preexisting trenches or edges. Moreover, most turns occur at an angle of 60° or 120°, and turn angles of 30° and 90° are occasionally observed. This gives strong support that the tailoring follows the graphene honeycomb lattice and opens the possibility for atomically precise fabrication of GNRs, equilateral triangle and trapezoid pieces. The reciprocating rectilinear movement of an NP can fabricate GNRs with smooth edges. Figure 3a shows a tailored GNR of ~2 μm in length. We consider that these turns are possibly related to the change of adhesive strength between the graphene edges and NPs,[7] which are important for the formation of GNRs and regular graphene pieces. (iii) It is interesting to find that the tailoring speed for SiO_x NPs is ~4 nm/s, which is much slower than that reported for metal NPs (e.g., 250 nm/s for Ag NPs[8]). The slower tailoring speed provides great potential for accurate control of the trench length or the length of the tailored GNRs. Furthermore, the catalytic activity of the SiO_x NPs can be maintained for a long time (more than 1 h, see SI). Combined with the fact that the same edge structure can be dominantly obtained for the same NP, as shown above, we believe that the long tailoring lifetime is useful for the fabrication of regular graphene nanostructures with the same edge structure.

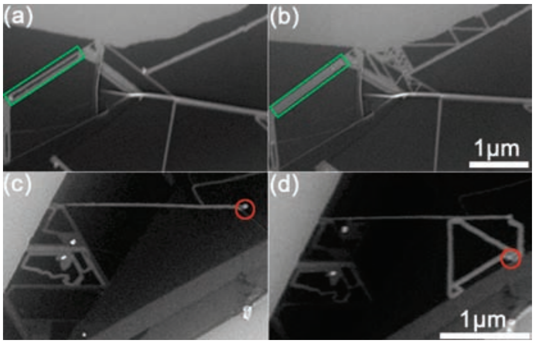

Figure 3. Tailoring of FLGs with annealing time. (a, c) SEM images of tailored FLGs by annealing for 10 min. (b, d) SEM image of the same FLGs in (a, c) tailored by annealing for another 10 min, totally 20 min. The denoted areas by green rectangle frames in (a) and (b) show the evolution of a tailored GNR, and the white dots denoted by red circles in (c) and (d) are the same NP.

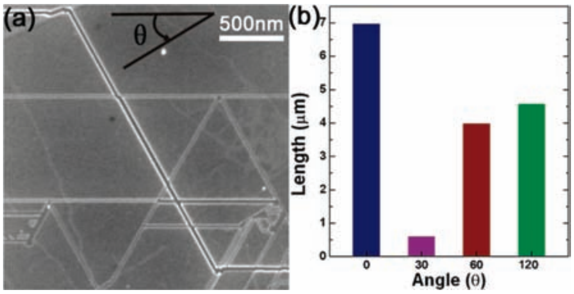

Figure 4. Selective tailoring of FLGs by SiO_x NPs. (a) SEM image of a tailored FLG with many trenches. We define horizontal orientation as 0°, and the angle θ is measured in anticlockwise direction. (b) The histogram of total tailored trench length versus trench angle from the SEM image (a).

Figure 4a shows a tailored FLG with many trenches of regular angles and smooth edges, and Figure 4b illustrates the measured trench lengths versus different trench angles. It is interesting to find that more than 95% of trenches are tailored along directions of 0°, 60°, and 120°, indicating that tailoring with preferential crystallographic direction can be realized by SiO_x NPs. This result is higher than that reported for metal NPs.[7,8] Due to the different interaction of graphene edges for different NPs, the different preferential tailoring direction can be expected for SiO_x NPs compared to metal NPs. Our preliminary results show that the narrower trenches (less than 30 nm) mostly have an armchair edge, while the wider ones (more than 100 nm) have a zigzag edge (see SI), which is in contrast to those tailored by Ni NPs.[8] Further studies are in progress, including the physical origin of the difference in tailoring by metal and nonmetal NPs and NPs with different sizes, which will provide valuable information for the controllable crystallographic tailoring of graphene by NPs.

Moreover, it is worth pointing out that the tailoring of FLGs by *in situ* formed SiO_x NPs can produce few-layer GNRs with different widths and the same orientation. Figure 5 shows typical SEM and AFM images of tailored FLGs, and many GNRs can be found, as denoted by arrows. The obtained few-layer GNRs have smooth edges, their length can reach several micrometers, and their width can be narrower than 10 nm. Interestingly, GNR junctions can also be fabricated by one NP, as denoted by green arrows in Figure 5c, which consists of a few GNRs with the same orientation and

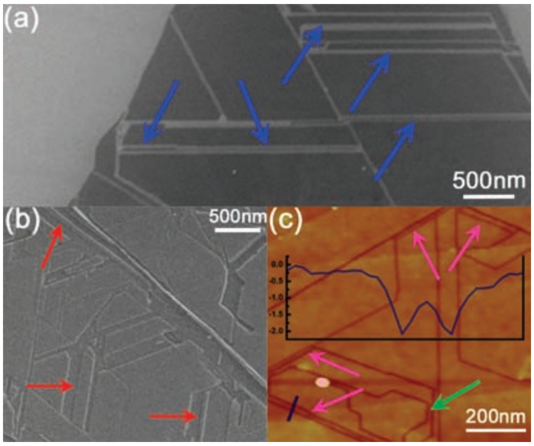

Figure 5. GNRs fabricated by tailoring of FLGs by SiO_x NPs, which are denoted by arrows. It can be found that the widths of some GNRs are narrower than 10 nm. The inset of (c) shows the height profile along the blue line, which reveals that the fabricated GNR is ~0.8 nm in thickness.

different widths. These results demonstrate that this method has potential for the fabrication of narrow GNRs and GNR junctions used for electronic and other applications, although it is still a big challenge to fabricate well-defined GNRs or graphene pieces. Further studies are required for accurate control of the tailored structure.

To validate the generality of SiO_x NPs toward tailoring, we prepared SiO_x NPs by using a film coating system and annealed HOPG with the as-prepared NPs (for details, see SI). Before annealing, we can see that many NPs are on the surface of HOPG and some of them are located at the edge of graphene with different layers. High resolution XPS (with a peak at 102.9 eV and O signal at 532.4 eV) analyses indicate that these NPs are SiO_x.[16] After annealing with the same conditions as those used for the tailoring of FLGs by *in situ* formed NPs, it can be found that many trenches with smooth edges are formed on the HOPG. Moreover, it is worth noting that the tailoring also proceeds along the preferential crystallographic direction. In addition, the XPS shows a similar peak at 103.2 eV, corresponding to the Si from SiO_x, which suggests that the composition of these NPs is not changed after the tailoring process. These results demonstrate the generality and repeatability of SiO_x NPs toward tailoring no matter where these NPs come from and indicate that no reaction occurs between the NPs and carbon atoms during the tailoring process.

On the basis of the above experimental results, the tailoring mechanism of FLGs by SiO_x NPs is proposed. We note that (i) the size of SiO_x NPs remains almost unchanged even as they keep tailoring for more than 10 μm long (see SI), indicating that there is no mass loss of NPs during the tailoring process. This is consistent with the above observations that no reaction occurs between the NPs and carbon atoms during the tailoring process, which provides strong evidence for the catalytic role of NPs in tailoring. (ii) The tailoring process does not work without the presence of SiO_x NPs and a H_2 atmosphere. Therefore, we suggest that the tailoring of FLGs by SiO_x NPs possibly occurs by a catalytic hydrogenation mechanism similar to that for tailoring by metal NPs of Fe and Ni.[6,7] The catalytic activity of SiO_x NPs is perhaps due to the quantum size effect of nanostructures.[18] At an elevated temperature, the carbon atoms at the edges first react with H_2 with the assistance of the neighboring NPs due to the high activity of edge atoms. Since it is energetically more favorable for the NPs to remain at the step edge, the NPs follow the receding edge.[9] Thus, the NP effectively tailors a trench in graphene. The anisotropic tailoring direction may be due to the anisotropy of the interaction of NPs with crystalline graphenes.[8] This finding will open up the possibility of using nonmetal NPs as a catalyst for the hydrogenation of carbon materials. In addition, SiO_2 films have been recently used for the growth of carbon nanotubes with methane as a carbon source and hydrogen as the carrier gas.[19] These results lead to an interesting subject on the role of SiO_x NPs in the conversion of hydrocarbons and graphitic materials with the assistance of hydrogen.

In summary, we find that nonmetal SiO_x NPs can tailor FLGs into GNRs and regular pieces with smooth edges. The tailoring of graphene is realized by the movements of the SiO_x NPs in an atmosphere of H_2, and the tailored trenches exhibit high selectivity of the crystallographic orientation compared to the reported metal NPs. The low tailoring rate and the long lifetime provide great potential for accurate control of the trench length or the length of the tailored GNRs. As a result, some smooth GNRs with a length of several micrometers and a width narrower than 10 nm are obtained. In addition, a catalytic hydrogenation mechanism is proposed for the tailoring of graphene by SiO_x NPs. These findings open up the possibility for atomically precise graphene device fabrication without metal contamination and indicate the potential catalytic activity of nonmetal NPs for the hydrogenation of carbon materials.

Acknowledgment. This work was supported by the MOST of China (No. 2006CB932701), NSFC (Nos. 50872136, 50972147, and 90606008), and CAS (No. KJCX2-YW-M01). We thank Prof. Xue Qikun, Ma Xucun, Wang Lili, Zhao Weiwei, and Wang Qingyan for the generous help of STM measurements.

Supporting Information Available: Experimental details, high resolution XPS results of SiO_x NPs, and effects of different tailoring conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA906610E