

## **Cobalt-Mediated Crystallographic Etching of Graphite** From Defects

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**H**erein is reported a study of Co-assisted crystallographic etching of graphite in hydrogen environment at temperatures above 750 °C. Unlike nanoparticle etching of graphite surface that leaves trenches, the Co could fill the hexagonal or triangular etchpits that progressively enlarge, before finally balling-up, leaving well-defined etched pits enclosed by edges oriented at 60° or 120° relative to each other. The morphology and chirality of the etched edges have been carefully studied by transmission electron microscopy and Raman analysis, the latter indicating zigzag edges. By introducing defects to the graphite using an oxygen plasma or by utilizing the edges of graphene/ graphite flakes (which are considered as defects), an ability to define the position of the etched edges is demonstrated. Based on these results, graphite strips are successfully etched from the edges and graphitic ribbons are fabricated which are enclosed by purely zigzag edges. These fabricated graphitic ribbons could potentially be isolated layer-by-layer and transferred to a device substrate for further processing into graphene nanoribbon transistors.

## 1. Introduction

Graphene nanoribbons (GNRs) have attracted considerable attention in recent years as they are considered as a promising alternative channel material to silicon for future field-effect transistors. Whereas graphene in itself

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is a zero-bandgap material,<sup>[1]</sup> narrow ribbons of graphene (GNRs) have been theoretically predicted to be semiconducting<sup>[2]</sup> with a bandgap that depends on the narrowness and chirality of the ribbon, as well as edge effects.<sup>[3]</sup> There are two basic strategies to fabricate graphene nanoribbons: bottom-up and top-down. Bottom-up approaches or, more specifically, chemical routes, can yield high quality GNRs with well-defined edges. For instance, GNRs with defined edge geometries can be synthesized through coupling of aromatic monomers.<sup>[4]</sup> Another example is the sonochemical method that produces GNRs through chemical exfoliation and sonication.<sup>[5]</sup> Field-effect transistors based on sub-10 nm GNRs from this method have been shown to exhibit high on-off ratios of about 107 at room temperature.<sup>[5]</sup> However, such material will need to be positioned accurately for subsequent processing into devices, a procedure that is highly challenging and does not appear to be scalable at the present time. On the other hand, the top-down approach covers diverse methodologies that can facilitate device integration.<sup>[6]</sup> Typical top-down methods like graphite surface modification induced by a constant bias on a scanning tunneling microscope (STM) tip,<sup>[7]</sup> graphene scratching<sup>[8]</sup>

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or local anodic oxidation<sup>[9,10]</sup> by atomic force microscope (AFM), oxygen plasma etching based on lithographic method using patterned resist<sup>[11]</sup> or even nanowires<sup>[12]</sup> as protective mask, precise etching using helium ion microscope (HeIM),<sup>[13]</sup> and unzipping carbon nanotube by direct plasma etching<sup>[14]</sup> or oxidation process.<sup>[15-17]</sup> have been explored for GNR fabrication. But low vield and difficulties in controlling the GNR positions and edge states limit the application of these top-down methods. In contrast, another top-down approach that involves direct patterning of highly oriented pyrolytic graphite (HOPG) followed by graphene layer isolation and placement methods, such as the transfer printing<sup>[18]</sup> and stamping,<sup>[19]</sup> opens a route to mass production of GNR devices.<sup>[20]</sup> Therefore, the development of wellcontrolled approaches to achieve graphitic ribbons with defined positions and edges, which is an ideal starting material for GNR device fabrication, is of timely importance. In this work, we report Co-mediated crystallographic etching of graphite which can be further exfoliated as graphene layers and transferred to a device substrate.

The etching of graphite has been intensively explored by researchers. Typically the etching processes convert the solid state graphite to gaseous carbon compounds. Several etchants can serve this purpose, such as oxygen,<sup>[21]</sup> hydrogen,<sup>[22]</sup> water,<sup>[23,24]</sup> and carbon dioxide.<sup>[23,24]</sup> The most obvious approach is thermal oxidation which, at certain pressures, has been observed to give rise to hexagonal etched pits on the surface of HOPG.<sup>[25]</sup> Plasma etching<sup>[26]</sup> is another effective approach to etch graphite. In combination with a protective mask, oxygen plasma is able to produce predefined graphite patterns,<sup>[27]</sup> but the etched edges are not atomically sharp. H<sub>2</sub> plasma is found to etch graphite and graphene anisotropically<sup>[28]</sup> and can thus pattern graphene into nanoribbons with zigzag edges.<sup>[29]</sup> This method provides for a pathway to GNR device fabrication starting from single-layer graphene. Along a different vein, the phenomenon<sup>[30]</sup> and mechanism<sup>[31]</sup> of catalytic hydrogenation of graphite had been studied decades ago. Catalytic hydrogenation usually initiates at the interfaces of nanoparticles (NPs) and graphite during high temperature annealing in a hydrogen environment.<sup>[30]</sup> The NPs move on the surface of graphite leaving etched trenches with smooth edges. Nanoparticles of different kinds of materials have been used to shape the surface of graphite or graphene, such as Fe,<sup>[32]</sup> Ni,<sup>[33]</sup> Ag,<sup>[34]</sup> Co,<sup>[35]</sup> and even SiO<sub>x</sub>.<sup>[36]</sup> However, it is hard to control the etching directions of these



**Figure 1.** a) Top view of Scanning Electron Microscope (SEM) image of a typical etched graphite surface. Scale bar: 1 µm. (FEI Nova NanoSEM 230 at 10 kV). b) 45° tilted SEM image. Scale bar: 500 nm. (FEI Nova NanoSEM 230 at 10 kV). c) TEM image of Co-etched graphite surface. Inset of c) is selected area electron diffraction of position indicated. Scale bar: 500 nm. (JEOL 2010F TEM at 200 kV). d) Higher magnification of the hexagonal Co in graphite. Scale bar: 100 nm. (JEOL 2010F TEM at 200 kV).

nanoparticles, which can turn randomly at 60° and 120° directions relative to the original trajectory. Moreover, the moving particle may re-deposit some carbon on the etched graphene edges of the trenches, which results in random chirality at the etched edges.<sup>[37]</sup> The approach taken in this article allows a top-down definition of where etching should take place in order to realize a particular graphitic ribbon structure. In this approach, the etch front of the metal particles on graphite/graphene, but on a much larger scale. As there is limited scope for carbon re-deposition, the quality of etched edges should be better than the graphene edges produced by metal particles.

### 2. Results and Discussion

## 2.1. Morphology and Structure of Natural Graphite Surface after Co-Mediated Etching

A thin Co film deposited on thick graphite is observed to etch the graphitic surface when it is heated above 750 °C in the presence of hydrogen at low-pressure. The etching is found to progress along fronts aligned along principal crystallographic directions of graphite leading to pits enclosed by edges oriented at  $60^{\circ}$  or  $120^{\circ}$  relative to each other, as indicated in **Figures 1**a,b. Some of the Co enclosed within the pits also ball-up and leave regular etched pits on the graphite surface. A statistical analysis on the angles between the etched edges showed an equal distribution of angles in multiples of 60°, and we did not observe any edges that are aligned to 30° directions from one of these principal directions, thus indicating that all the etched edges must be of the same chirality.<sup>[38]</sup> By controlling the pre- and post-annealing profile (see S1 of the Supporting Information (SI)), the metal film breaks up into islands rather than nanoparticles, and etching is only initiated at certain sites on the graphite surface. In some cases, the Co etches the graphite and extends to fill the etching pits (see S2 of the SI). This phenomenon may lead to the crystallographic patterning of graphene layers and thus deserves further investigation.

To study in detail the crystallinity and epitaxial relationship between Co and graphite of the etched structure, we characterized the samples in a transmission electron microscope (TEM). Figures 1c,d show a typical Co-etched graphite surface where the edge acuity of the etched graphite layers appears to be excellent. In addition, we carefully examined the etched edges over an area of ~50 nm<sup>2</sup> in the TEM, and the edges still look sharp and smooth at this magnification for both Co-graphite junction and the etched graphite edge after the Co had been retracted through a balling-up process (see S3 of SI). Selected area electron diffraction (SAED) was then carried out with an electron beam diameter of 200 nm at locations that enclose both Co and graphite (Figure 1c inset). The primary hexagonal set of diffraction pattern represents the graphite. There is a second set of dots adjacent to the graphitic diffraction pattern where the lattice spacing is measured to be 0.25 nm (calibrated by the in-plane lattice



Figure 2. a) AFM image and typical height profile on etched graphite surface. Scale bar: 500 nm. b) AFM image and typical height profile isolated and transferred graphene layers from etched graphite surface. Scale bar: 500 nm.

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**Figure 3.** a) and b) SEM image of graphite surface etched at 800 °C for 20 s and 40 s, respectively. Scale bar: 1  $\mu$ m. c) Typical balling-up stage (800 °C for 40 s). Scale bar; 300 nm. d) Co balling-up on unetched surface (800 °C for 40 s). Scale bar: 1  $\mu$ m. (Nova NanoSEM 230 at 10 kV).

spacing 0.246 nm of graphite<sup>[39]</sup>) which is close to the value of Co(0001) surface (lattice mismatch < 2%<sup>[40]</sup>). From these diffraction patterns, we can conclude that the Co patches filling the etching pits are single crystal and epitaxially aligned with the graphitic surface, with a slight lattice mismatch when observed at room temperature.

Atomic Force Microscope (AFM) measurements of the etch pits after balling-up of the metal (**Figure 2**a) show that tens of graphene layers have been totally removed while the underlying surface is planar to within 1–2 atomic layers. The small roughness in the height profile is actually at the limit of the accuracy of the measurement, and provides evidence that the etching stops at certain depth. By sampling 30 positions on different graphite pieces on one typical sample, the etched pit depth was found to be in the range from 10 to 22 nm. If the graphite is sufficiently thin, the Co can etch through to the substrate and leave polygonal through-holes in the graphite.

The Co could be removed by acid and then the etched graphene layers could be isolated and transferred to other substrates using micromechanical cleavage method by Scotch tape. Figure 2b shows graphene layers with etched pits transferred onto a  $Si/SiO_2$  substrate. The thickness of the indicated graphitic layers in Figure 2b is measured to be 2.57 nm

which is significantly smaller than the typical depth of etched pits in the original sample, demonstrating that this graphite flake originated from the top layers of the etched graphite surface. In addition, prepatterned structures on HOPG could be transferred by transfer-printing technique.<sup>[18]</sup> The prepatterned graphite could be attached to some media material, such as gold film,<sup>[41]</sup> and be exfoliated and transferred to arbitrary substrates during a printing step. An alternative way is to directly stamp the pre-patterned graphite on to another substrate.<sup>[19]</sup> Furthermore, this stamping process could be assisted by electrostatic force for thinner product.<sup>[42]</sup> Both of these printing and stamping processes could be repeated for many times yielding the same single or few layer graphene patterns, which favors the mass production of graphene devices.

#### 2.2. Mechanism of Co-Mediated Graphite Etching

The etching mechanism is now considered. During the annealing, the Co film shows a remarkable morphology change at 750 °C (see S2 of SI), which is due to the melting of the Co film. Peng et al. demonstrated that thick-film (>4 molecular layers) melting erupts along grain boundaries



Figure 4. a-d) Schematic of the formation of the structure in (e). e) Side view of an etched pit. Scale bar: 30 nm. (JEOL 2010F TEM at 200 kV).

in polycrystalline solid films at certain temperature  $T_{\rm m}$ forming liquid 'strips'.<sup>[43]</sup> The solid–liquid interfaces propagate<sup>[44]</sup> when the temperature is higher than  $T_{\rm m}$  and thus the Co film reaches a solid-liquid coexistence regime (~50% in volume fraction).<sup>[43]</sup> Further increase in temperature leads to liquid-phase Co containing many small crystalline patches, which is not considered to be in coexistence.<sup>[43]</sup> Under our experimental conditions (750–950 °C), the Co film is likely to be at this stage. Once the Co film breaks into isolated islands, it can be compared with the melting of metal nanoparticles. A similar phenomenon has been studied for the state of metal catalyst particles during carbon nanotube growth. The melting temperature of nanoparticles is depressed by the Gibbs-Thomson effect and by the formation of a eutectic with carbon.<sup>[45]</sup> The melting point of Co nanoparticles ~30 nm in size is only 600 °C in a carbon-containing environment.<sup>[46]</sup> The existence of liquid-phase of catalyst particles during carbon nanotube growth has been experimentally detected.<sup>[47]</sup> However, the liquefaction may not have occurred homogeneously in this carbon-induced liquefaction as described by Harutyunyan et al.<sup>[47]</sup> There might be some solid content in the middle of the Co islands even during the etching, but the Co at the progressive etching front (near Co-carbon interfaces at the etching edges) should be liquid, as observed for nanoparticle etching.<sup>[48]</sup>

During annealing, the Co islands migrate on the surface of the graphite and etching only initiates at certain locations on the graphite surface. The natural defects on the graphite surface represent preferential sites at which etching initiates. A similar phenomenon was found by Shi et al. where the anisotropic etching only initiates at the step edge as well as at defect sites when they used hydrogen plasma to etch graphene.<sup>[28]</sup> The surface defects of HOPG are known to bond the metal atoms strongly and form nucleation centers<sup>[49]</sup> so that the drifting Co islands will be pinned at the defective sites. Because the defect sites are more reactive due to the existence of dangling bonds or lattice distortion,<sup>[28]</sup> etching then starts from the defects. To explore the evolution of this etching phenomenon and the effect of defects, defects

were systematically introduced to the graphite surface. We spin-coated a layer of PMMA on the peeled graphite flakes and patterned a matrix of open holes (~1.5 µm in diameter) by electron beam lithography (EBL). The PMMA acted as a protective layer during a light oxygen plasma treatment in a reactive-ion etching system (10 W RF power, 17 V substrate bias, for 10-20 seconds) to introduce defects at the exposed areas of the graphite surface. A 100 nm Co film was then deposited and lifted off, to create circles (1.5 µm in diameter) of Co over the plasma-exposed graphite. After annealing the samples at 750 °C for 60 seconds in a chemical vapor deposition (CVD) chamber filled with a 1:2 mixture of H<sub>2</sub> and Ar (total gas flow rate of 200 sccm at a pressure of 20 Torr) to reduce any Co oxide, we increased the temperature to 800 °C in 20 s with other conditions unchanged and maintained for either 20 s or 40 s to perform the etching. This relatively lower temperature should lead to slower etching which allows us to capture the different stages of etching. In an attempt to freeze the shapes of most of the Co for further investigation, the sample was guenched to below 500 °C within a second by shutting down the heater power. As shown in Figures 3a,b, while etching did not start simultaneously for all Co circles, the trend is clear. A Co circle balls-up quickly during the early stage of annealing without etching (Position A) and then starts to etch the graphite surface (Position B). The Co extends to progressively etch the surrounding graphite (Positions C and D). Finally, the Co balls-up leaving a regular etched pit (Position E). Position F shows a rare case where the Co film breaks up. This could possibly be due to rapid contraction during the quenching process. Figure 3c shows a higher magnification SEM image of a typical etched pit where the Co balled-up at the centre, which demonstrates that the Co could cleanly detach from the etched edges.

Defects introduced by the  $O_2$  plasma are essential for initiating the etching. In a control experiment where Co circles were deposited without plasma treatment, the metal circles were found to ball-up without etching under the same conditions (800 °C, 40s) as shown in Figure 3d. Observations on a larger matrix of Co circles (see S4 of SI) reveal



**Figure 5.** a) Schematic of selectively etched many-layer graphene with armchair edge (Case A) and zigzag edge (Case B) by Co. b) SEM image of a typical etched sample. Scale bar: 500 nm. c) Raman spectrum taken at positions indicated in b). d) Schematic of FLG strip originally defined by oxygen plasma prior to etching by Co film at positions indicated; e) Raman map showing the intensity of G-peak, and f) D-peak.

that Co only etches the graphite surface at locations with natural defects or edges. The preferential location of Co dots at defect sites is clearly seen in some cases. This comparison supports our hypothesis that defects are the starting points of the etching phenomenon. Natural defects on graphite surface should play the same role when a continuous Co film is used. As it is heated up, the Co film melts and breaks up into isolated islands. The melted Co balls migrate on defectfree graphite surface but tend to be pinned at surface defects. The etching starts and liquid Co extends to progressively etch the graphite. The etching follows a chemical process which is the same as found in nanoparticle etching of graphene, with metals such as Fe<sup>[32]</sup> and Ni.<sup>[33]</sup> The crystallographic etching of graphite is based on the catalytic gasification of carbon in a hydrogen atmosphere forming methane via the following reaction:<sup>[50]</sup> C(solid) + 2H<sub>2</sub>(gas)  $\rightarrow$  CH<sub>4</sub>(gas). In this reaction, the Co serves as a catalyst. Actually, the metal-particle etching of graphite has been studied in detail in the 1970s.<sup>[51]</sup> However, in our experiments, the amount of Co used is considerably greater, allowing the formation of balls and shapes other than particles and results in relatively larger etched pits filled with Co. A tensile force on the liquid Co is exerted from the evolving edges being etched, the origin of which should be the same as the driving force which induces particles to move along the etching channels in metal-particle etching. As discussed by Tomita et al., this force is much larger than the van der Waals force between metal and the carbon atoms on a basal plane.<sup>[30]</sup> There are several possible origins of such a directional force. In their discussion of crystallographic etching, Datta et al. suggested that crystallographic etching could be due to the favorable adhesion and wetting of the molten metal to the graphene edge along specific crystallographic directions.<sup>[32,48]</sup> Another possible mechanism is crystallographic dependence of the (metal particle)-graphene reactivity. In other words, the reaction of carbon and hydrogen to form methane has lower activation energy along specific directions commensurate with the few layer graphene (FLG) lattice.<sup>[32]</sup> The work of Schäffel et al. also suggested that the metal near the edge of a graphene layer interacts with the dangling bonds at the edge. This interaction is stronger than with the underlying graphene sheet. Once the hydrogenation reaction starts, the nanoparticle tends to maintain maximum contact with the step edge.<sup>[50]</sup> All these possible mechanisms are also applicable in explaining our experimental results.

When the etching starts, the Co melts and extends to fill the etching pits because of the pulling force from the edges, which is balanced by the Co surface tension. This equilibrium could be disturbed and lead to Co detachment and balling-up by fluctuations in the local environment, such as a variation in temperature or new defects encountered during the etching progress. Even in the absence of perturbations, the Co would not extend for ever due to its finite volume (a cross-section TEM study of Co filling the etched pits is reported in S5 of the SI). Hence Co balls are observed only after prolonged annealing under etching conditions (see S2 of the SI). As the pits become larger, the surface of the Co becomes concave, as a result of which the force from the surface tension tends to tear the Co from the graphitic edges (Figures 4a,b). This force may cause the detachment of the Co from the etching edges of the graphite. As the Co balls-up due to surface tension, the etched pits are exposed. In some cases, the Co ball is found to be attached to one of the edges (Figure 4e). This may arise from balled-up Co drifting on the basal plane of the etched pit until it meets an edge (Figures 4c,d), or inhomogeneous detachment from different edges of the pit. During cooling down, the arrangement of Co atoms is influenced by the underlying graphitic surface and the metal recrystallizes as an epitaxially aligned single-crystal, in a process similar to that observed for silver particles coalesced on HOPG following annealing at 50 °C for days.<sup>[52]</sup>

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### 2.3. Realization and Raman Spectrum Analysis of Graphitic Ribbon

As discussed above, defects are the initiation sites for the etching and the edges of graphite may be considered as defects. Based on the chirality of the natural edges, two kinds of etching shapes may be expected (Figure 5a). For case A, a graphite strip with zigzag edges should have a triangular etching front with an enclosed angle of 120° (see S6a of the SI). Whereas for case B, a graphite strip with armchair edges, the etching pattern will become a trapezium (see S6b of the SI). From a different perspective, these two etching patterns are a part of a hexagon rotated relative to each other by 30°. The etching mechanism could be exploited in the fabrication of graphene nanoribbons. We started with multilayered graphite (around 60 layers) that can be etched through to the substrate and yet is sufficiently thick enough to provide adequate pulling forces from the edges being etched. The graphite flake was patterned, using an electron beam lithography process followed by oxygen plasma etching, into long strips of ~1 µm width (see S7 of the SI) aligned parallel to a natural edge of the flake so that the edges of the strips should be roughly parallel to either an armchair or zigzag edge direction. Co circles of 1 µm diameter and 100 nm thickness were then deposited at the edge to etch the graphene layers. Compared to edges produced by O<sub>2</sub> plasma from SEM images, the Co-etched edge is much smoother, as shown in Figure 5b. In order to gain insight into the chirality of the edge of such many-layered graphene etched by Co, Raman analysis was performed on

the structure as fabricated. Raman spectroscopy was carried out on a WITecCRM200 Raman system with 532 nm (2.33 eV) excitation and laser power at the sample below 0.1 mW to avoid laser-induced heating.<sup>[53]</sup> The diameter of the focused laser spot is ~500 nm and Raman spectra were taken at positions indicated in Figure 5b. The intensity ratio of the D band to the G band  $(I_D/I_G)$  is much higher at the edge that had been etched by  $O_2$  plasma than at the edge formed by Co etching (Figure 5c). Since the D peak located around 1351 cm<sup>-1</sup> reveals the structural defects of such material, the defect level of Co-etched edge is significantly lower than the edge produced by oxygen plasma etching which is known to introduce structural disorder<sup>[3]</sup> and amorphization at the etched edge of graphene layers.<sup>[54]</sup> By using this method, we successfully fabricated a ribbon structure around 100 nm in width as shown in Figure 5d.



**Figure 6.** a) Co on peeled few-layer graphene strip. Scale bar: 5 µm. b) Higher magnification SEM image of (a) after etching. Scale bar: 1 µm. c) Peeled single-layer graphene. Scale bar: 10 µm. d) After O<sub>2</sub> plasma, Co deposited before etching as indicated. Scale bar: 10 µm. e,f) Raman map showing the intensity of G-peak and D-peak of etched single-layer graphene in (d) (top graphene strip) after etching. Scale bar: 1 µm.

We performed Raman mapping of intensity of G-peak (Figure 5e) and D-peak (Figure 5f) with dwell time of 1 second and step size of 200 nm. In Figure 5e, the map of G peak indicates there is a ribbon structure between two parts of the belt structure. In Figure 5f, there are D peak signals at the edges produced by O<sub>2</sub> plasma while there is almost no D peak intensity at the edges fabricated by Co etching. This result suggests the Co-etched edge is a zigzag edge of low defect<sup>[55]</sup> because any existence of armchair segments along  $\pm 30^{\circ}$  with respect to the zigzag edge direction would present an observable D peak.<sup>[56,57]</sup> Note that our sample contains around 60 layers of graphene, which means that the Co had cut through the entire stack of graphene layers with sub-nm roughness or better. In this experiment, the gap between the two adjacent Co circles deposited to etch the graphene layer is around 200 nm, and the width can

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possibly be reduced to a much narrower range by starting with a smaller gap width. Although our single-layer resist electron beam lithography process to create relatively thick Co catalyst films with gaps narrower than 200 nm is limited to wider separations, this result provides a demonstration of the potential of this approach to produce ribbons at defined positions.

To demonstrate the potential of our method in shaping few- and single-layer graphene, we repeated the same process with peeled few-layer graphene and single-layer graphene flakes (Figures 6a-d). Since the pulling forces to balance the surface tension of Co decrease as the number of graphene layers reduces, it is difficult for Co catalysts to extend significantly towards the middle of the strip during etching. Hence we patterned the Co catalysts into trapezoidal patterns as shown in Figure 6a. From SEM images (Figure 6b), although the starting shape of the Co film strongly influences the final pattern of the etched graphene, the etched edges do not always follow the shape of the patterned Co catalyst precisely. Based on the phenomenon observed, we postulate that when the number of graphene layers is insufficient, the Co will detach gradually but not uniformly from the edge of the graphene layers due to the low collective pulling force from the edge. Nevertheless, the D peaks at the Co-etched edges are still quite weak in the Raman map even for single-layer graphene (Figure 6c–f) which is similar to the case where many-layer graphene was etched, as shown in Figure 5. Although the etched few- and single- layer graphene edges may not always appear to be straight, they should be composed by small saw tooth structures with  $60^{\circ}$  or  $120^{\circ}$  turns. All the edges should share the same zigzag chirality.<sup>[38]</sup> Figures 6e,f clearly demonstrates that the quality of Co-etched edges (both sides of the narrower ribbon part around 150 nm in width) are better than those fabricated by the conventional e-beam lithography/ O<sub>2</sub> plasma approach, as indicated by the significantly lower Raman D-peak intensity.

### 3. Conclusion

In conclusion, we observed how relatively larger amount of Co etches the graphene layers in graphite. The morphology and chirality of the etched edges have been carefully studied. By applying the phenomenon and etching mechanism proposed, we successfully fabricated graphitic ribbon structure composed by purely zigzag edges. The high selectivity of the chirality of etching edges and the ability to pre-determine the etching positions could potentially be applied to the fabrication of graphene ribbons through the development of an improved isolation and transfer technique to a device substrate.

## 4. Experimental Section

*Etching Graphite by Co Thin Film*: In this work, graphite flakes were first mechanically exfoliated onto an 5 mm by 5 mm oxidized Si substrate with 285 nm thick SiO<sub>2</sub>. After annealing in forming gas

(5% H<sub>2</sub> and 95% Ar at total pressure 10 Torr) at 400 °C for 1 hour to remove tape residue, a 10 nm Co film was deposited onto the sample by thermal evaporation. The prepared sample was then placed on a thin rigid carbon heater (5 mm wide, 100 mm long, and 0.5 mm thick) of low thermal mass in a CVD chamber filled with a 1:2 mixture of H<sub>2</sub> and Ar at a total gas flow rate of 200 sccm at a pressure of 20 Torr.

*TEM Sample Preparation*: For top view, the sample was spincoated with a 600 nm thick polymethylmethacrylate (PMMA) layer and baked at 120 °C in an oven for 30 min to improve the adhesion of the PMMA to the graphite pieces. After immersion in a 45 wt% KOH solution at room temperature for about 2 hours, the PMMA membrane detached from the substrate and was transferred on a lacey carbon TEM grid. The PMMA layer was then removed by acetone.<sup>[58]</sup> For side view, we used a focused ion beam (FIB) to crosssection some of the Co pits after deposition of a protective layer (Pt or SiO<sub>2</sub>). The lamellae were then transferred to a TEM grid by Omniprobe for further viewing.

## Supporting Information

*Supporting Information is available from the Wiley Online Library or from the author.* 

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