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Etched nanoholes in graphitic surfaces for enhanced electrochemistry of basal plane

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ABSTRACT

The understanding and tailoring of the electrochemistry of graphite is of significant industrial importance. We develop a method of etching pits into the basal planes of highly oriented pyrolytic graphite (HOPG) by electrolyzing the substrate. The etching of HOPG was realized by performing electrochemical reactions at alternating potentials at room temperature, and the resulting membranes are characterized using atomic force microscopy, scanning electron microscopy, X-ray photoelectron spectra, X-ray diffraction, Raman spectroscopy, Fourier transform infrared spectroscopy, and cyclic voltammetry. Etching only occurs when the electrolysis at negative bias is followed by a brief switch to a positive bias. The size of the etched pits can be tuned by varying applied potential and reaction time, with deeper pits formed with increased redox cycles and reaction time. Cyclic voltammetry reveals that the electrochemical performance is enhanced greatly as etching progresses due to exposure of edge sites. For its ease of application, efficiency and low cost, our wet etching approach has great promise as a method to develop high active electrodes and nanoporous membranes at large scales for various industrial applications.

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1. Introduction

Nanoporous materials have grown in importance for various applications in filtration [1], catalysis [2], energy storage [3], and particularly biomedical technologies such as DNA sequencing [4, 5] and protein detection to single-molecule resolution.^[6] Nanoporous materials have even been proposed to be used as “molecular corrals” in which nanoscale chemical reactions can occur in a contained fashion [7, 8]. Although biological nanopores are commercially available, their short lifetimes, fixed sizes and requirement of a bio-compatible environment restrict their potential for wider applications. On the other hand, solid-state nanopores are considered more desirable, since they can be fabricated with tunable sizes, chemical and mechanical properties, allowing them to overcome many of the downsides associated with biological nanopores [9].

The introduction of graphitic materials has proven to be very exciting for the development of nanoporous materials. These materials are not only strong, but can be easily modified to a form that is selectively impermeable to ions or even gases [10-13], making them especially well suited for filtration applications. Although excellent filtration often comes at the expense of low throughput, water can flow on graphitic substrates with very little friction [14-16]. The combination of durability, high throughput, electrical conductivity and many other remarkable properties of graphitic materials, along with its low cost, makes nanoporous graphitic materials highly desirable[17-19]. Beyond their filtration capabilities, nanoporous graphite is already widely used as anode materials for Li-ion [20] and Na-ion batteries [21], because the pores increase the charging and discharging rate capability, cyclability, and Coulombic efficiency. Additionally, the porosity allocates space for the growth of silicon nanowires and facilitates enhanced electron transport efficiency and electrochemical performance [22].

Previously, several etching techniques have been developed to etch pits into the basal planes of graphite. The cleanest and most popular of these techniques involves the gasification of graphite by hyperthermal treatment with air [23] or molecular oxygen [24], oxygen plasma [25], and hydrogen plasma [26-28]. These reactions take place at high temperatures and require special devices. Alternatively, it is also possible to etch graphite chemically, yet typical protocols require high concentrations of strong alkalis and acids, and long reaction hours [20]. These methods are therefore complicated to implement and are neither energy nor cost effective. Herein, we demonstrate a method to etch highly oriented pyrolytic graphite (HOPG) through a two-step electrochemical reaction that is simple and rapid, while requiring only inexpensive and readily available reagents.

2. Experimental

2.1. Electrochemical etching process

Highly ordered pyrolytic graphite (HOPG) (ZYG grade, SPI) was used as a working electrode. An Ag/AgCl reference electrode, and Platinum (Pt) auxiliary electrode were obtained from CH Instruments, USA. HOPG was cleaved with Scotch® Tape (3M) before each experiment. A wire was glued to the HOPG using silver epoxy and then insulated by AB glue and cured for 2 days at room temperature. The HOPG surfaces were then mounted onto the atomic force microscope (AFM) stage. An aliquot of 100 μ L sodium carbonate (10 mM, pH $\sim$ 11) was dispensed on HOPG surfaces. The Pt counter electrode was then dipped into the droplet.

For ease of reference, we define a standard potential in which pores are etched into the graphite. We will then later describe how modifications to the protocol lead to changes in the efficacy of etching. In the standard protocol, a negative bias of -1 V was first applied to HOPG for 10 min, before the etching was produced by alternating the bias to a positive potential of 5 V for 5 s. The procedures for the standard protocol are listed in Table 1.

2.2. AFM measurement

AFM characterization was performed with a Bioscope Catalyst AFM (Bruker). Height images were captured in ScanAsyst mode under manual control. V-shaped silicon cantilevers (SNL-10 A, Bruker) with a nominal spring constant of 0.35 N/m were used. The treated electrodes were imaged in solutions or in air. In our previous report, no difference of the same scan area was found between in liquids and in air [29]. In the current study, at a large bias of ~ 5 V, micrometer gas bubbles formed and resulted in AFM imaging impossible in liquids. To image the surface after reactions, liquids were removed and AFM characterizations were done in air. For example, in the case of sample 1, after a negative potential of -1 V applied to HOPG for 10 min, the height image was collected in solutions to ensure that the surface was clean. A positive potential (~ 5 V) was then applied to the working electrode. To check the outcome of the etching process, the electrolytes on the HOPG were removed and the surfaces were washed with Milli-Q water (Millipore Corporation, Boston, MA) for three times, and then blown dry with a stream of nitrogen. Finally, the surfaces were scanned again in air with AFM.

2.3. Cyclic voltammetry measurement

Cyclic voltammetry experiments were carried out on a μ Autolab type III electrochemical analyzer (Eco Chemie, The Netherlands) connected to a computer and controlled by the NOVA Version 1.8 software (Eco Chemie). Electrochemical experiments were carried out in a droplet at room temperature

with a three-electrode configuration (Ag/AgCl/1.0 M KCl as the reference, Pt as the auxiliary). Cyclic voltammetry experiments were conducted in the presence of 10 mM $[\text{Fe}(\text{CN})_6]^{4-/3-}$, at a scan rate of 100 mV s⁻¹ in a supporting electrolyte of 50 mM phosphate buffer solution (pH 7.2). The supporting electrolyte was purged with nitrogen for 20 min before electrochemical measurements. All the electrochemical potentials in this paper are stated with respect to an Ag/AgCl/1.0 M KCl reference electrode. Both newly cleaved and etched HOPG surfaces were tested. The k^0 of HET was calculated using the Nicholson method [30]. The roughness factor was not taken into account. The diffusion coefficient $D = 7.26 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for $[\text{Fe}(\text{CN})_6]^{3-/4-}$ was used.

2.4. Characterizations

A JEOL 6700F field-emission scanning electron microscope (SEM) was used to acquire the SEM images at 5.0 kV at a working distance of 8 mm. The HOPG surfaces were fixed onto a carbon tape on an aluminum SEM holder for analyses. X-ray diffractometry (XRD, Smartlab, Rigaku Co.) was carried out at room temperature at a scan rate of 2°/min with an X-ray source of Cu K α ($\lambda = 0.1541 \text{ nm}$) at 40 kV and 30 mA. The XPS measurements were performed with a VG ESCALAB 220i-XL spectrometer using a monochromatic Al K α source (1486.6 eV). Raman spectra were obtained with a confocal micro-Raman LabRam HR spectrometer (Horiba Scientific) using an argon ion laser beam ($\lambda = 532 \text{ nm}$) employing backscattering geometry with a CCD detector. Fourier transform infrared spectroscopy (ATR-FTIR, Perkin Elmer 100) was used to characterize the surface of treated HOPG.

3. Results and discussion

3.1. Electrochemical etching of HOPG

The etching process was checked by AFM characterization and the results are summarized in Table 1. No etching was found in the one-step electrochemical reaction for sample 2 – 4 for both negative bias and positive bias. At a bias of 5 V (sample 3) or – 5 V (sample 4), the bubbles are generated between the surface graphene layers by electrolyzing the previously intercalated species, causing delamination from the substrate. This is in consistent with our previous report [29]. Etching was found in two-step reactions (samples 1, 5, and 11): the first reduction and followed by oxidation. All the two-step reactions started with oxidation shows no etching effects. The influence of changing the sequence of the applied bias on etching was performed (samples 1, and 8 – 10). AFM images of samples 8 – 10 were shown in Figure S1. The results suggest that the reduction plays an important role in etching, while the applied positive bias and time during oxidation is also important.

Table 1. Electrochemical reactions in 10 mM Na₂CO₃ electrolytes.

Sample	1	2	3	4	5	6	7	8	9	10	11
1 st step	-1V	-1V	5V	-5V	-1V	-1V	-1V	1V	-1V	1V	-5V
	10min	10min	5s	5s	10min	10min	10min	10min	10min	10min	5s
2 nd step	5V	—	—	—	5V	4V	5V	-5V	-5V	5V	5V
	5s	—	—	—	10s	30s	1s	5s	5s	5s	10s
Etching	√	—	—	—	√	—	—	—	—	—	√

Our electrochemical etching protocol involves performing electrolysis on electrolyte-immersed HOPG with alternating potentials. In a successful etching process (sample 1), the HOPG is first subjected to a relatively long reduction step (applied negative potential - 1 V for 10 min) and then followed by a very brief oxidation step (positive potential 5 V for 5 s). Atomic force microscopy (AFM) height images show clear differences between reduction and oxidation (Figure 1). As the electrolysis of water also leads to the formation of gaseous bubbles on the substrate, the sample has to be dried in order to observe what happens to the substrate after etching. Figure 1a showed that the surfaces are smooth after reduction at - 1 V for 10 min. Etching pits appeared after oxidation at 5 V for 5 s (Figure 1b, and Figure S2 SEM image). The pits can reach as deep as 30 nm, while their lateral sizes may extend up to 1 μ m.

Figure 1. AFM height images of HOPG during etching. (a) The image was captured in 10 mM Na₂CO₃ electrolyte after application of negative potential (sample 2, -1V 10 min). (b) Image of sample 1 was captured in air, the liquids were removed after etching reactions (continuing sample 2, 2nd step 5 V 5 s) at the same scan area as in (a), although there is a slight drift from the original imaging area. Scan size: 10 μ m $\times$ 10 μ m; height scale: 50 nm.

137 Let us define the two steps (1st step: -1 V for 10 min, and 2nd step: $+5$ V for 5 s) involved in this
 138 reaction as one redox cycle. To observe how the etching is influenced by redox cycle, we now show
 139 systematically how the morphology of the pits changes under modifications to the standard protocol by
 140 increasing the number of redox cycles and increasing the oxidation time. Figure 2 shows AFM height
 141 images of the etched surface after 3 and 5 redox cycles. When the number of reaction cycles increases,
 142 we found that the overall etching area increases (as indicated by white arrows in Figure 2). The pits
 143 become wider and deeper, as well. We show in Figure 3 the depth distribution of pits under 1, 3 and 5
 144 redox cycles, and the mean depths are 25, 98 and 140 nm respectively. Increasing the oxidization time
 145 in the second step can also increase the etched area and depth of pits (Figure 3, figure 4c). By increasing
 146 the duration of the second oxidation step from 5 to 10 s (Sample 5), we find that the mean depth of
 147 etched pits increased from 30 to 40 nm. with a lateral size of up to 1 μ m. The surface area to volume
 148 ratio data for the etched pits was listed in Table S1. The increase in both the number of reaction cycles
 149 and oxidation time in the second step reduce the surface area to volume ratio for the etched pits, which
 150 indicates the surface area to volume ratio increase for the electrodes.

151
 152 Figure 2. AFM height images of HOPG in air after 3-cycle (a) and 5-cycle (b) etching in 10 mM
 153 Na_2CO_3 solutions at the same scan area. Arrows point to a pit expand laterally after 2 more cycles'
 154 etching. Scan size: 20 μ m $\times$ 20 μ m; height scale: 200 nm. (c) and (d) are cross-sectional profiles of the
 155 scan lines as drawn in (a) and (b) respectively. In comparison, the profile in (d) shows wider and deeper
 156 pits.

Figure 3. The depth of pits distribution and Gaussian fit for 1-cycle (sample 1), 1-cycle but oxidation of 10 s (sample 5), 3-cycle, and 5-cycle etching. Gaussian parameters: 1-cycle: mean = 25, Gaussian width = 6.6; 1-cycle 10 s: mean = 40, Gaussian width = 14.8; 3-cycle: mean = 98, Gaussian width = 19.6; 5-cycle: mean = 140, Gaussian width = 40. The AFM images were processed in Gwyddion, a modular program for scanning probe microscopy data visualization and analysis. The images were inverted, shift minimum data to zero, and analyzed using the height distribution function. The normalization of the densities $\rho(h)$ (where h is the corresponding height) is such that $\int_{-\infty}^{\infty} \rho(h)dh = 1$.

3.2. Influence of reaction voltage and time

As described in Table 1, samples 1, 5, 6, and 7 all follows the similar two-step electrochemical reaction protocol, while sample 6 and 7 did not show etching. The results indicate the applied bias and reaction time during the oxidation step are critical for the etching process. When the second step potential was reduced to 4 V, we did not observe any pits, even when the reaction was carried out for a relatively long time of 30 s (Figure 4a, sample 6). At the standard 5 V, we find that pits were not formed for a short 1- second burst (Figure 4b, sample 7), but started to appear once the reaction time was increased beyond 5 s. We note that some blisters were present at potentials above 2 V, but these were no longer visible at 5 V when the reaction time was increased beyond 5 s (Figure 4c).

The results show that the etching suddenly occurs at a critical potential, and gradually proceeds above the critical potential. It suggests that there is an energy barrier for the electrochemical etching process. During the oxidation step at a bias below 5 V, bubbles appeared. The bubbles are generated between the surface graphene layers by electrolyzing the previously intercalated species, causing delamination from the substrate [29]. Note that there is no possibility of confusing the blisters with surface-attached bubbles, since the scans here are imaged in air, and before imaging, liquid and any bubbles attached on top of the substrate are removed upon drying the substrate. When the second step is performed at a bias of 5 V, blisters formed (at 1 s) and then suddenly disappear (at 5 s) and pits formed on the surface.

However, we cannot definitively conclude that bubble formation is a necessary condition for etching, since the repeat experiments shown in figure 2 indicate that the pits are etched gradually.

Figure 4. AFM height images collected in air by varying the second step in the redox cycle. For all the experiments, a negative potential -1 V 10min was applied in the first step. Different positive potential was applied in second step (a) 4 V for 30 s (sample 6), (b) 5 V for 1 s (sample 7), and (c) 5 V for 10 s (sample 5). Intercalated bubbles were observed for potential below 5 V. Pits appeared at 5 V 5 s, and become deeper and larger at 5 V 10 s. Scan size: $20\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$; height scale: 100 nm.

In a trial experiment (sample 11) we perform the first step at a negative bias of -5 V for 5 s, followed by a positive bias of 5 V for 10 s. The results are similar, yielding wider and deeper etched pits with a rougher surface (Figure S3). The data indicates that the reaction time may be significantly reduced to ~ 10 s.

3.3. Influence of electrolytes

The influence of electrolytes on etching is shown in the supplementary information (Figure S4). Milli-Q, 10 mM KOH, and 10 mM NaCl solutions were used as electrolytes. A few intercalated bubbles were formed in Milli-Q water (Figure S4a). A few etched pits and wrinkles appeared in the case of 10 mM KOH (Figure S4b). Relatively large intercalated bubbles formed in the case of 10 mM NaCl (Figure S4c). Further study showed etched pits in 100 mM KOH (Figure S5). Etched pits were created when the electrolysis was performed in two steps: a negative bias of -1 V applied to HOPG for 10 min; a positive bias of 5 V applied to HOPG for 5 s (Figure S5a). It was surprising that etching occurred during one step reaction where only a positive bias of 5 V is applied to HOPG for 5 s (Figure S5b). However, the intercalated blisters formed as well. No etching was found in only one step electrolysis on HOPG anodes in other electrolytes.

The presence of ions is essential for the etching process. Etching does not take place in Milli-Q water, perhaps because of the low current transfer efficiency in the absence of electrolytes. In NaCl solutions, not only does O^{2-} participate in reactions at the HOPG electrode, but Cl_2 may also form when Cl^- is neutralized. Cl^- and O^{2-} compete during the oxidation, thus limiting the etching process by oxygen oxidation.

3.4. Spectroscopic characterization

In order to understand the etching process, spectroscopic measurements via X-ray photoelectron spectra (XPS), X-ray diffraction (XRD), Raman techniques and infrared spectroscopy were carried out. The etched graphite was characterized by XPS and XRD, as shown in Figure 5. Figure 5a shows the Gaussian fitting in the high-resolution XPS spectrum presented in the region of C 1s. The peak at 284.8 eV can be assigned to C-C carbon, while the other two peaks are due to the contributions from oxygen functionalities. The peak at 286.2 eV can be assigned to hydroxyl groups, and the one at 288.5 eV is assigned to carboxyl groups [31]. The contribution of carbonyl groups around 287 eV is negligible. In figure 5b, the (002) peak at 26.5° were found for both pristine graphite and etched graphite, which indicates an interlayer spacing of 0.34 nm [32]. The etching process on graphite flakes exfoliated by a Scotch tape also showed similar XRD peaks. The reduced intensity of (002) diffraction peak in the XRD pattern of etched HOPG clearly demonstrates that although the d-space is not changed, the HOPG has been exfoliated to some extent during the etching process, which is caused by intercalation and gas generation.

Figure 5. (a) High-resolution XPS spectrum and Gaussian fitting results of the C 1s.(b) XRD patterns of etched HOPG and pristine HOPG.

Figure 6. ATR-FTIR spectra of etched HOPG (sample1) and pristine HOPG.

Figure 6 shows the FTIR spectra of HOPG and etched HOPG. In comparison, the etched HOPG sample shows a strong broad peak around 3507 (3300 –3600), which could be attributed to the OH stretching vibrations. The peaks observed at 1735 cm^{-1} is ascribed to C=O stretching [33, 34]. Another strong broad peak is observed above 1660 cm^{-1} , which is assigned to OH groups [35, 36]. This indicates that an electrochemical anodic etching event has occurred, where sp^2 carbons in HOPG have been cleaved and oxygenated groups have been introduced. The appearance of the oxygenated groups in the XPS data such as C=O and C–O groups, indicate the increase of defect sites that can be made available for electron transfer [37]. While anodic oxidation increases in the oxygenated groups may result in repulsion between the electrode surface with the negatively-charged ferro/ferricyanide [38, 39], the clear increase in the amount of defect sites is reflected by the improvement of the electron transfer as described in Figure 8 (see reference [40]). The density of defect sites present in the electrochemically etched HOPG was investigated using Raman spectroscopy in Figure 7.

Figure 7. Raman spectra of etched HOPG (a), and pristine HOPG (b). Raman spectra showed D, G, and 2D peaks. The G band for etched HOPG samples was numerically fitted by two peaks (G and D'). The 2D band was deconvolved into two peaks by Lorentz fitting (2D₁ and 2D₂).

Two distinct bands (G and D) are usually observable in the Raman spectra of graphitic materials. The D band is due to amorphous sp³ domains in carbon layers, while the G band is distinct due to sp² in-plane vibrations. In our case, the pristine graphite barely shows a D peak, but a sharp G peak at 1584 cm⁻¹ (Figure 7b) due to its well-ordered structures. The 2D peak is around 2700 cm⁻¹, which was numerically fitted by two Lorentzian line shapes (2D₁ peak at 2684 cm⁻¹ and 2D₂ peak at 2724 cm⁻¹). The Raman spectra of etched HOPG are quite different from graphene nanobubble formed by water splitting with only positive bias or negative bias [29]. The D band is found at 1347 cm⁻¹ very strong and broad. Then the first order G peak was deconvolved into two Lorentz peaks, G band (1580 cm⁻¹) and D' band (1616 cm⁻¹). The 2D peak was fitted by two Lorentzian peak 2D₁ (2680 cm⁻¹) and 2D₂ (2714 cm⁻¹).

The integrated intensity ratios I_D/I_G , $I_{D'}/I_G$, I_{2D1}/I_{2D2} , and I_{2D}/I_G are indicators of the presence of crystalline defects and are listed in Table 2. For the pristine HOPG, the ratios I_D/I_G and $I_{D'}/I_G$ are close to zero due to its well-ordered crystalline structure. For etched HOPG, the value I_D/I_G is 1.98 and $I_{D'}/I_G$ is 0.1. I_{2D}/I_G (0.26) reduces to a third of the pristine HOPG (0.74). The I_{2D1}/I_{2D2} (11.86) of the etched HOPG is clearly different from that of the pristine HOPG (0.35).

Table 2. The position and intensity of D, G, D' and 2D bands in the Raman spectra of pristine HOPG and etched HOPG (sample 4).

	D band (cm ⁻¹)	G band (cm ⁻¹)	I _D /I _G	D' band (cm ⁻¹)	I _{D'} /I _G	2D ₁ band (cm ⁻¹)	2D ₂ band (cm ⁻¹)	I _{2D1} /I _{2D2}
HOPG	1351	1584	0.01	-	-	2684	2724	0.35
Etched HOPG	1347	1580	1.98	1616	0.1	2680	2714	11.86

265

266 Table 3. Peak to peak separation (ΔE_p) and the corresponding heterogeneous electron transfer rate.

267

	Pristine HOPG	²⁾ Sample 1	³⁾ Sample 2	⁴⁾ Sample 3	⁵⁾ Sample 4
ΔE_p (V)	0.760	0.190	0.683	0.298	0.640
STD	0.0070	0.0185	0.0285	0.0175	0.0485
number of runs	3	3	3	3	3
ψ	5.74×10^{-5}	1.34×10^{-1}	1.66×10^{-4}	3.09×10^{-2}	2.95×10^{-4}
¹⁾ k^0 (cm s ⁻¹)	5.41×10^{-7}	1.26×10^{-3}	1.56×10^{-6}	2.91×10^{-4}	2.78×10^{-6}

268

269 ¹⁾ $K^0 = \frac{\Psi}{(\pi D_o \frac{nFv}{RT})^{1/2}}$, where D_o is diffusion coefficient, n is number of electrons, F is Faraday constant, v

270 is scan rate, R is gas constant, T is temperature in K , and ψ is the function can be calculated from ΔE_p
 271 [30, 41].

272 ^{2)- 5)} Samples 1 - 4 as described in Table 1.

273 ²⁾ Sample 1 is for two-step reactions: 1st step at a negative potential of -1 V for 10 min, and 2nd step at a
 274 positive potential of 5 V for 5s. ³⁾ Sample 2: 1 step reaction at -1 V 10 min; ⁴⁾ Sample 3: 1 step reaction
 275 at 5V 5s; ⁵⁾ Sample 4: 1 step reaction at -5V 5s.

276

277 3.5. Enhancing heterogeneous electron transfer rate

278 Cyclic voltammetry is a useful electrochemical method to study the heterogeneous electron transfer
 279 (HET) from the solid to the solution phase and the corresponding interactions between the electrode's
 280 surface and the solvated redox probe. In this investigation, the electrochemical probe of
 281 ferro/ferricyanide is used to establish the HET of the highly ordered pyrolytic graphite before and after
 282 electrochemical etching, due to changes in surface properties. The study was carried out with 10 mM

283 ferro/ferricyanide in the presence of 50 mM phosphate buffer. Using the peak-to-peak separations (ΔE_p),
 284 the HET can be calculated (Table 3) [30].

285

286 Figure 8. Cyclic voltammetric signature of treated samples and pristine HOPG, recorded in the presence
 287 of 10 mM $[\text{Fe}(\text{CN})_6]^{4-/3-}$. Conditions: scan rate 100 mV s^{-1} , background electrolyte 50 mM phosphate
 288 buffer solution (H 7.2). Etched HOPG samples treated by two-step reactions: sample 1 (1st step: -1 V
 289 10 min , and 2nd step: $5 \text{ V } 5 \text{ s}$) and sample 5 (1st step: $-1 \text{ V } 10 \text{ min}$, and 2nd step: $5 \text{ V } 10 \text{ s}$). Samples 2-4
 290 are treated by one-step reactions: sample 2 ($-1 \text{ V } 10 \text{ min}$), sample 3 ($5 \text{ V } 5 \text{ s}$), and sample 4 ($-5 \text{ V } 5 \text{ s}$).

291 As depicted in Figure 8, HOPG has the lowest electron transfer rate ($\Delta E_p = 0.760 \text{ V}$; $5.41 \times 10^{-7} \text{ cm s}^{-1}$)
 292 ¹). In the pristine HOPG electrode, only the basal plane of the HOPG was exposed to the
 293 electrochemical probe in solution, where a few edge planes were available for electron transfer [40, 42,
 294 43]. The electron transfer rate is superior at the edges and defect sites, but sluggish at the basal plane
 295 [43]. This results in a slow heterogeneous electron transfer rate. Electrochemical treatments were then
 296 carried out and the corresponding cyclic voltammetric measurements were measured to investigate the
 297 effects on the changes of surface properties with the corresponding influence on HET.

298 For electrochemical treatments, potentials of 5 V and -5 V were chosen, where oxygen (sample 3) and
 299 hydrogen bubbles (sample 4) are evolved on graphite respectively. On the electrochemical activation at
 300 a negative bias of -5 V for 5 s , there is an increase in electron transfer rate from 5.74×10^{-7} to 2.78×10^{-6}
 301 cm s^{-1} (Figure 8). This increment is due to the increase in surface area of the electrode due to the
 302 exposition of new carbon surfaces, arising from the delamination of graphene layers as hydrogen gases
 303 are released from the electrochemical reduction of protons [44-46]. However, the electrochemical

304 activation for 5 V for 5 s results in two orders of magnitude increase in electron transfer rate, from 5.41
305 $\times 10^{-7}$ to $2.91 \times 10^{-4} \text{ cm s}^{-1}$. This is due to the ability of the anodic potential to evolve oxygen bubbles for
306 etching the surface of the HOPG, producing defects that are made available for heterogeneous electron
307 transfer, with a concomitant increase in the surface area [37, 38, 47]. This was exhibited by Zhang and
308 colleagues [37], where anodic treatment on HOPG resulted in the exposition of new defect sites on the
309 HOPG and increased the surface area. Conversely, a low potential treatment of the HOPG at -1 V for
310 10 min, exhibited a similar effect as in the case where a potential of -5 V for 5 s was held, where
311 hydrogen evolution reaction results in a slight increase in new carbon surfaces in HOPG [44-46]. This
312 leads to a negligible change in the electron transfer rate, and clearly showcases the need for the positive
313 potential during the activation of the electrode surface area, towards HET.

314 The sequential treatment of the electrode surface for -1 V for 10 min and the sequential step of 5 V
315 for 5 s (sample 1) for the investigation of electron transfer, results in the best electron transfer rate, with
316 an improvement of three orders of magnitude, from 5.41×10^{-7} to $1.26 \times 10^{-3} \text{ cm s}^{-1}$. This can be
317 attributed to the accompanying increase in the surface area and the introduction of defects in the
318 structure of the HOPG [48]. This combination is directly proportional to the effects observed during
319 hydrogen evolution and oxygen evolution reactions, where the coupling of the increase in surface area at
320 cathodic potentials, followed by an anodic electrochemical etching process greatly increased the effect.
321 Both elongation reaction time and increase the number of redox cycle can increase the etched volume
322 when the pits become wider and deeper, resulting in a decrease of surface-area-to-volume ratio of the
323 etched pits. The surface-area-to-volume ratio data for the etched pits (Table S1) suggest that the increase
324 in volume is faster than the surface area during etching. A smaller surface-area-to-volume ratio of pits
325 means a bigger specific area of the graphite electrodes, and thus a better electrochemical performance.
326 The etched pits with higher depth expose a larger number of layers and higher density of edge active
327 sites, and are found to exhibit superior electrochemical properties. This is evident as higher peak current
328 shown in cyclic voltammetric curve. Our results are supported by Banks [49] and Brownson's work
329 [50], that the electrochemical response is dependent on the density of edge plane sites and influenced by
330 the coverage of defects and the number of graphene layers.

331 The increase of defects from the anodic electrochemical etching has increased the number of defects
332 in the HOPG system. The density of defects increased dramatically, as can be seen in the ratio of I_D/I_G ,
333 which increased from 0.01 to 1.98. This increased the number of defect sites, where facile electron
334 transfer can take place [51]. As a result, there is a correlation between crystalline defects and the

335 electrochemical performance of the HOPG after etching, towards the electrochemical probe of
336 $[\text{Fe}(\text{CN})_6]^{4-/3-}$. While there has been an increase in negatively charged oxygenated groups after the
337 electrochemical treatment in the etched HOPG in comparison to pristine HOPG, as illustrated in Figure
338 7, this has not diminished the performance of the materials towards electron transfer in $[\text{Fe}(\text{CN})_6]^{4-/3-}$.
339 This suggested that an alternative factor is responsible for the increase in heterogeneous electron transfer
340 rate [40]. The use of anodic potentials to produce oxygen bubbles to etch laminar graphitic structures
341 has increased the number of defect sites on the HOPG and exposed the new carbon surfaces on the
342 electrode to be available for electron transfer [37]. The Raman spectra in Figure 7 illustrates this effect.
343 The increase in the I_D band at 1350 cm s^{-1} is characteristic of the graphitic edge planes and defect sites
344 of anodically etched HOPG, with the heterogeneous transfer rate increase being proportional to the
345 density of these sites [39].

346 Although the mechanisms of etching still remain unclear during the electrochemical reactions, we
347 have nevertheless demonstrated that the sequence of biasing applied to the graphite plays an important
348 role. Zheng et al. found that carbon nanocrystals released electrochemically from graphite during
349 potential scanning in phosphate buffer solution [52]. They suggest that carbon nanodots were initially
350 immobilized in porous graphite, and were electrochemically oxidized to water soluble particles. We
351 cannot support this view, given that we do not find etched pits on HOPG surfaces simply under positive
352 or negative bias, except in 100 mM KOH solutions.

353 Instead, we hypothesize that a by-product is formed during electrolysis with a negative potential
354 which subsequently attacks the substrate when the polarity is switched to a positive potential. Previous
355 reports suggest that electrolytes can become intercalated between graphite layers when a bias is applied
356 to HOPG [53]. The dissolved oxygen in the solutions was reduced to OH^- ($2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \rightarrow 4\text{OH}^-$, at
357 a potential of 0.4 V) when HOPG was used as a cathode. Enrichment of OH^- in between the HOPG top
358 layers and the high pH of electrolytes make the following oxidation process ($4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^-$)
359 attack the HOPG blister layers from both top and below surfaces at the same time, which leads to C-C
360 bond breakage. Our hypothesis of C-C bond breakage is supported by XPS results of the C-OH and
361 COOH groups on the etched HOPG surfaces. The results from one step oxidation at the anode of 5V in
362 100 mM KOH solutions supports our hypothesis. In this case, 100 mM KOH electrolytes are of high pH
363 ~ 13 and the intercalation of OH^- takes place at a positive bias, which makes the oxidation on both sides
364 at the intercalation positions possible. The gas evolution will be quicker than the etching if inadequate
365 concentrations of OH^- become intercalated (Figure S5b). The etching mechanism in 100 mM may be

366 similar to Delannay's model that C-C bond breaks in the presence of KOH in steam gasification [54]. The
367 etching of graphene with a H₂-plasma has been reported [28]. Yang et al. ascribed the etching process to
368 hydrogenation and volatilization of reactive carbon sites by hydrogen radicals. The H-radicals attack the
369 carbon atoms and form C-H covalent bonds and the following oxidation will attach the reactive sites to
370 break the C-C bonds. According to Delannay's model, there will be one-carbon compound formed,
371 therefore the etching in Na₂CO₃ electrolytes may also form HCOOH or CH₃OH, an issue we are
372 interested in exploring in future work.

373

374 4. Conclusions

375 In this study, we have developed an electrochemical method to etch sub-micro holes on HOPG
376 surfaces. By alternating the applied potential, from negative (− 5 V) to positive (5 V), etch pits are
377 produced on HOPG surfaces. The etching time varies with the reaction parameters like the electrolytes
378 and the applied potential, and pits of 50 nm in depth can be etched over timescales as short as 10
379 seconds. Characterisation with various modes of microscopy and spectroscopy provide a clear account
380 of the physical and chemical changes to the graphite substrate during the etching process. AFM
381 measurements demonstrate that increasing the reaction time causes the pits are etched wider and deeper.
382 XPS data suggest that carboxyl and hydroxyl groups attached to the etched HOPG, which is backed up
383 by the FTIR study. Finally, the Raman spectra and a drop in the intensity of (002) diffraction peak in
384 XRD pattern of etched HOPG reveal that the HOPG has been exfoliated to some extent during the
385 etching process, which is caused by intercalation and gas generation. Our electrochemical method of
386 etching pits into graphite is appealing compared to traditional alternatives because it does not need
387 molecular hydrogen and oxygen, specific devices, or extreme conditions. It is simple, cost-effective and
388 easy to run only with several dry batteries and diluted sodium carbonate solutions required. For these
389 reasons, we anticipate that our protocol will find promising applications in material and electronic
390 engineering in the near future.

391

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