



Enhancement of adsorption on graphite (HOPG) by modification of surface chemical functionality and morphology

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Received 23 October 2001; accepted 30 March 2002

Abstract

The effects of chemical functional groups and surface morphology on the adsorption/desorption behavior of a model non-polar organic adsorbate (propane) on model carbonaceous surfaces [air-cleaved highly oriented pyrolytic graphite (HOPG) and plasma-oxidized HOPG], were investigated using temperature-programmed desorption (TPD). Oxygen- and hydrogen-containing functional groups exist on both air-cleaved HOPG and plasma-oxidized HOPG. The presence of these groups almost completely suppresses propane adsorption at 90 K. However, these groups can be removed from both air-cleaved and plasma-oxidized HOPG by thermal treatment (>500 K), leading to more than an order of magnitude increase in adsorption capacity. It is essential for both air-cleaved HOPG and plasma-oxidized HOPG to be outgassed at over 1273 K for all the adsorption sites to be chemically accessible for propane molecules. The effect of morphological heterogeneity is evident for plasma-oxidized HOPG as this substrate provides greater surface area available for adsorption, as well as higher energy binding sites.

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Keywords: A. Highly oriented graphite; B. Surface treatment; C. Temperature programmed desorption (TPD); D. Functional groups

1. Introduction

In spite of the importance of carbonaceous materials, our understanding of the role that the chemical and morphological characteristics of the surface play in surface related properties is less developed compared to our understanding of other materials. Unequivocal characterization of the chemical properties of carbon surfaces lags behind that of other surfaces due to the complexity of carbon surfaces compared to many other materials. The surface properties of carbonaceous materials are important for a number of applications. Carbonaceous surfaces are employed as supports for metal catalysts. They also show catalytic activity themselves [1]. For example, carbon is

the primary catalyst for the synthesis of phosgene (Cl_2CO) from carbon monoxide and chlorine [1,2]. The interaction of lubricants with the amorphous hard carbon film that protects magnetic data storage media plays an important role in their function [3,4]. Adsorption on carbonaceous surfaces is a ubiquitous atmospheric process [5,6]. It is also important for the environmental control of a variety of hazardous materials by adsorption, e.g., gas-phase mercury [7]. Understanding adsorption on carbon nanotubes, which has been shown to modify their electrical properties, is important for potential applications [8,9].

High surface area nanoporous carbon materials are characterized by high chemical and morphological heterogeneity. These characteristics affect their adsorption capacity, kinetics, and catalytic activity [1,10]. Therefore, understanding the chemistry and physics of carbonaceous surfaces may enable optimization of their function and usefulness [11]. For example, oxidation of activated carbon by nitric acid creates acidic groups on the surface, hindering alkane adsorption [12]. It is also well known that activated carbon surfaces chemisorb oxygen at low tem-

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perature, forming oxygen-containing functional groups [13]. The oxygen-containing functional groups, removed by outgassing above 500 K, can either enhance or reduce the adsorption capacity of microporous carbon depending on the specific adsorbate [14–16]. The presence of functional groups also modifies other carbon properties. For example, when activated carbon is used as a support for Pt catalysts, the dispersion of Pt increases as the concentration of oxygen functional groups on the carbon surface increases [17], because of electrostatic interactions [18,19]. The high surface area provided by morphological heterogeneity is one feature that makes carbonaceous materials useful for adsorption purposes. In general, higher surface area provides more adsorption sites leading to higher adsorption capacity [20]. However, the role of the morphological heterogeneity of carbon surfaces is not clearly understood and is still a subject of intense study [21–24].

This paper reports on the adsorption and desorption of a model adsorbate representative of non-polar organic compounds (propane) on model carbonaceous surfaces (HOPG). Both air-cleaved and plasma-oxidized HOPGs were studied to elucidate the effect of chemical functional groups and surface morphology on the adsorption/desorption behavior. This approach has the potential to provide a better understanding of the adsorption and desorption characteristics of carbonaceous surfaces that contain chemical and morphological heterogeneity. HOPG is frequently used as a substrate for scanning probe microscopy because it is easy to prepare and provides atomically large flat terraces [25]. It is generally assumed that cleaving in air provides a “clean” surface containing only carbon atoms in the hexagonal lattice and that only adventitious physisorbed impurities perturb the surface. Nevertheless, most authors report thermal treatment of HOPG over 700 K to clean the surface before UHV experiments [25,26]. The adsorption of alkanes on HOPG has been extensively investigated in the past by scanning tunneling microscopy (STM) [27], temperature-programmed desorption (TPD) [28], ellipsometry [29], neutron scattering [30], and differential scanning calorimetry (DSC) and neutron diffraction [31]. HOPG is typically modeled as containing only sp^2 carbon atoms, with no other functional groups present [32,33]. To our knowledge, there has been no report of the effects of oxygen-containing HOPG functionality on adsorption. Most investigations annealed HOPG to >1000 K and would not see the effects reported here. The results presented herein suggest that this may be an over-simplification and show that functionality present on air-cleaved HOPG significantly affects adsorption of a simple alkane, propane. The results of this study also have implication for the use of HOPG as a substrate in STM experiments.

Chemical and topological surface heterogeneity induced by oxygen plasma treatment provides means to explore high surface area and topologically heterogeneous carbonaceous surfaces used in technological applications.

2. Experimental

A stainless steel ultra high vacuum (UHV) chamber, pumped by a turbomolecular pump backed by a mechanical pump, provides a base pressure of 5×10^{-10} Torr after bakeout (1 Torr = 133.322 Pa). The chamber is equipped with a Bayard–Alpert type nude ion gauge and a quadrupole mass spectrometry (QMS) system (AccuQuad300, Stanford Research System) to measure total and partial pressure in the chamber. The QMS probe is housed in a stainless steel shield with a 2.5 mm diameter aperture [34]. The QMS system and shield assembly can be repeatedly located to within <1 mm of the sample for TPD experiments. This configuration ensures the collection of molecules from the sample surface alone during TPD. Retraction of the QMS and shield assembly up to 20 mm by a movable bellows device allows for sample rotation and adsorbate exposure [34].

A custom-made sample holder, depicted schematically in Fig. 1, that allows for the cooling and independent heating of two samples was used in these experiments. This enables sample comparison under almost identical conditions. The dual sample holder consists of two pairs of copper supports. The sample holder can be rotated around the z -axis by a sample manipulator (MDC, Model RMTG-275). A pair of supports is mechanically mounted on each side of a copper (OFHC) block welded on a stainless steel liquid nitrogen reservoir. Each copper support is electrically isolated from the others by sapphire disc (Meller Optics, Model MSW087/020A) in order to allow individual heating of each sample. Samples are mounted on the copper supports with stainless steel screws and Ta support plates.

Two $10 \times 10 \times 0.25$ mm HOPG samples (Grade SPI-1, SPI Supplies) were used to produce air-cleaved HOPG (a-HOPG) and plasma-oxidized HOPG (p-HOPG) samples. Air-cleaved HOPG was produced by peeling away topmost layers using scotch tape. The plasma oxidation was performed for 20 min in a plasma generator (Super Plasmod, March Instrument) at 1 mbar O_2 pressure and 100 W power. Prior to installation in the UHV chamber the samples were imaged by atomic force microscopy (AFM; Pico SPM, Molecular Imaging) in air using the contact mode. Samples can be cooled to 88 K with liquid N_2 and resistively heated to 1323 K. K-type thermocouples were spot-welded to the Ta support plates, and wedged against each of the samples. Research grade propane (Matheson Tri-Gas) was used as supplied. Dosing is performed by backfilling the chamber. Exposures are reported in Langmuir units ($1 \text{ L} = 10^{-6}$ Torr s), determined by uncorrected ion gauge readings. A constant temperature ramping rate, typically 2.5 K/s, is applied during a TPD experiment while partial pressure and sample temperature are measured using a personal computer equipped with an A/D board controlled by a customized LabView program. The

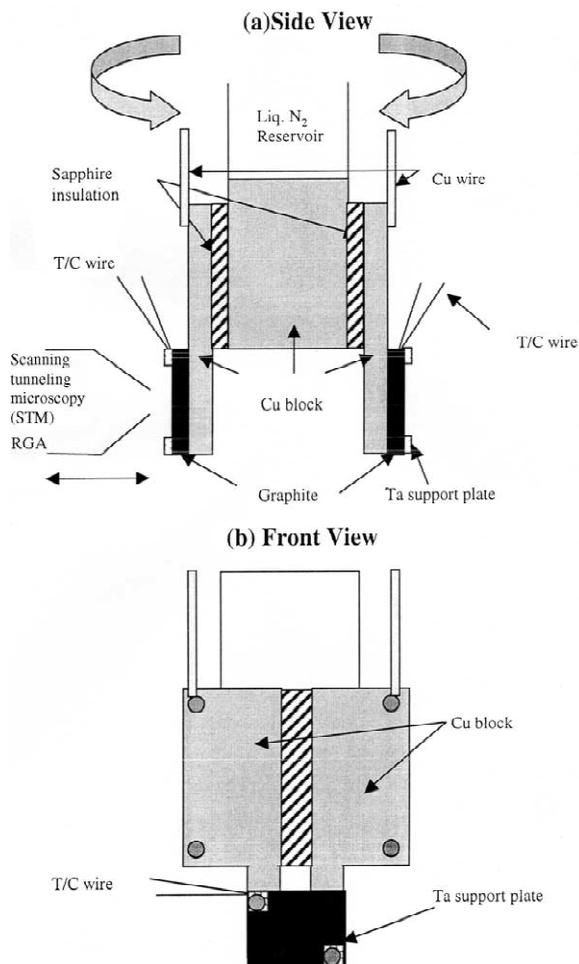


Fig. 1. Schematic view of the dual sample mount: (a) side view and (b) front view.

sample was observed through a viewport to glow with a uniform color, suggesting that it is uniformly heated. In addition, the narrowness of the propane TPD peaks (<10 K) supports uniform sample heating.

Essentially similar results to those reported herein were obtained using a different HOPG sample manufactured by a different company (Grade ZYA, Advanced Ceramics). This suggests that the experimental observations reflect intrinsic properties of HOPG.

3. Results and discussion

3.1. Air-cleaved HOPG

The gas evolution profiles as a function of temperature during surface heat treatment analysis of a-HOPG are displayed in Fig. 2. Heat treatment clearly leads to

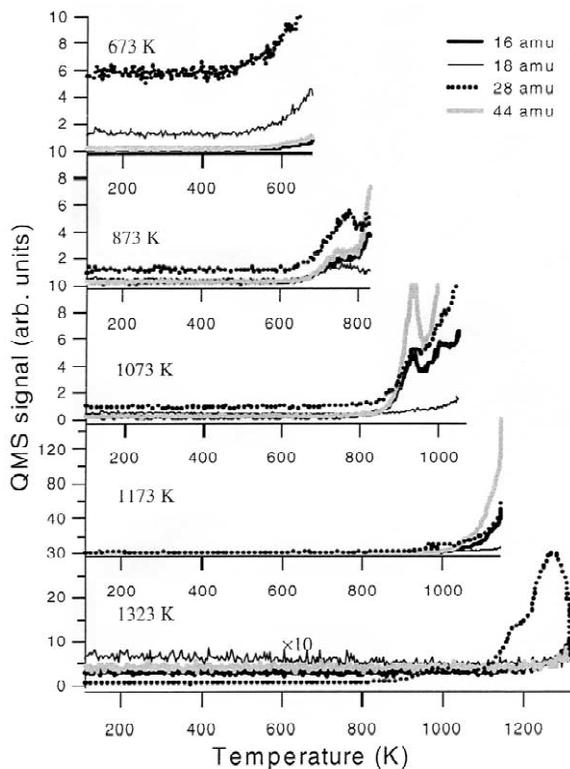


Fig. 2. Evolution of 16, 18, 28 and 44 amu signals during initial substrate heat treatment of air-cleaved HOPG to different temperatures. Data for 16, 18 and 44 amu in the 1323 K scan is multiplied by 10 to aid in viewing.

desorption of 16, 18, 28 and 44 atomic mass unit (amu) containing species, probably H_2O , CO and CO_2 related compounds, at temperatures above 500 K. It can be seen that there is no re-appearance of these features in the ~24 h that elapse between each successive heat treatment. The gas evolution only starts at temperatures higher than previous day's maximum treatment temperature. This result can be compared to the study of thermal desorption of CO and CO_2 from the heterogeneous surface of activated carbon [35]. It was found that the decomposition of the surface oxides on carbon occurs at temperature above 520 K and that outgassing above 1273 K is required to remove essentially all functional groups. In order to verify that gas desorption during heat treatment originated from the HOPG samples and not other parts of the sample holder, control experiments were performed where the air-cleaved HOPG sample was replaced by a gold coated Ta sample ($10 \times 10 \times 0.05$ mm). Heat treatment to over 873 K resulted in no significant gas desorption.

Fig. 3 shows a series of TPD spectra for propane dosed at 90 K on air-cleaved HOPG following heat treatment to various temperatures. A peak appears around 115 K in all cases and saturates at 3 L for 673 K, 7 L for 873 K and 8 L

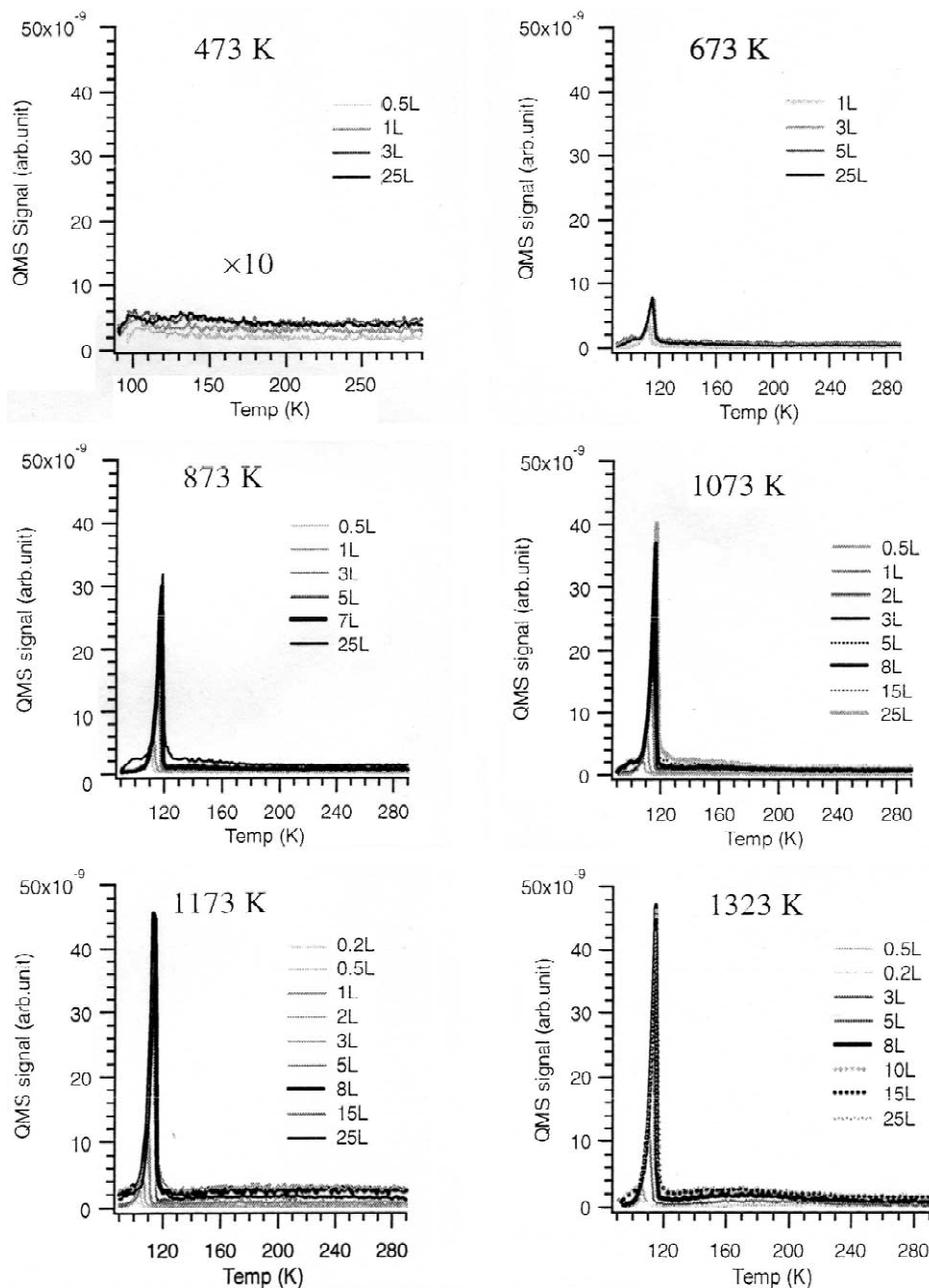


Fig. 3. TPD spectra at 29 m/e (propane) for air-cleaved HOPG after substrate heat treatment at various temperatures. Note that identical vertical scales are used for all figures. Data for 473 K is multiplied by 10 to aid in viewing.

for 1073 K and higher heat treatments, respectively. The TPD peak for air-cleaved HOPG treated at 473 K is barely detectable even when multiplied by 10 on this scale. As the heat treatment temperature increases, the propane TPD desorption peak height increases at equivalent exposure levels.

Fig. 4 illustrates the integrated TPD areas, corresponding to the relative amount of propane molecules

adsorbed at 25 L exposure for air-cleaved HOPG and plasma-oxidized HOPG, as a function of heat treatment temperature. A 25 L exposure results in saturation for all heat treatments reported here. The results depicted in Fig. 2 suggest that oxygen- and hydrogen-containing functional groups exist on the air-cleaved HOPG surface and that they are removed by thermal treatment. The results shown in Figs. 3 and 4 suggest that the removal of these

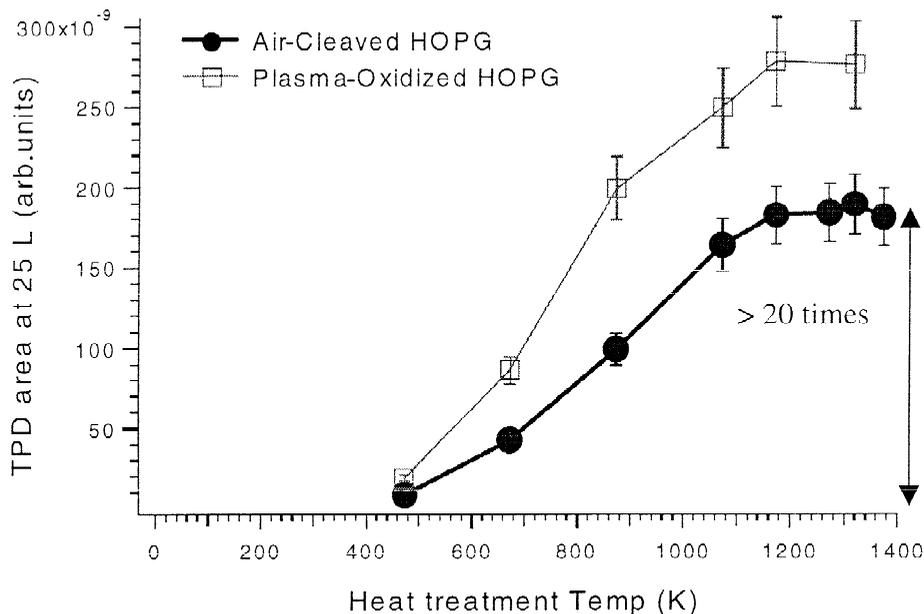


Fig. 4. TPD areas for 25 L exposure as a function of substrate heat treatment temperature for air-cleaved HOPG.

functional groups increases the number of chemically accessible adsorption sites for propane molecules. The results also suggest that propane, a non-polar organic, has an unfavorable interaction with the naturally existing polar functional groups on air-cleaved HOPG prior to heat treatment. The saturation of the adsorption uptake seen in Fig. 4 for outgassing temperatures above 1173 K suggests that heat treatment at $T \geq 1173$ K is needed to clean the air-cleaved HOPG surface for alkane adsorption.

Exposure to laboratory air for 24 h results in the reappearance on HOPG of similar types and quantities of functional groups as had been removed by heat treatment of air cleaved HOPG. This is revealed by the observation that the surface capacity for propane adsorption is initially low and that heating to 1273 K results in evolution of the same fragments as observed from air cleaved HOPG, resulting in, once again, a factor of 20 increase in propane adsorption capacity. This suggests that the surface functionality results from the interaction of the freshly cleaved or vacuum heat treated surface with air.

Propane TPD spectra grow with a common leading edge for all heat treatments, indicating zero order desorption [36]. Using zero order desorption kinetics, the activation energy for propane desorption from HOPG is estimated to be 30 ± 2 kJ/mol, which is in reasonable agreement with other studies of *n*-alkane adsorption on HOPG [28]. Uncertainties arise in part from the accuracy of temperature measurements. The location of the thermocouple in our experimental system is restricted by the fact that it cannot be spot-welded to HOPG. The calculated activation energy is about 25% greater than the heat of vaporization of propane, 23.9 kJ/mol, at 100 K [37,38]. The observa-

tions that the shape of the TPD spectra do not change with heat treatment temperature, the increasing propane uptake subsequent to each heat treatment temperature, and the invariance of the activation energy with each heat treatment step verifies that little adsorption occurs at 90 K at sites blocked by surface functional groups. It is very likely that these groups on HOPG are polar species (e.g., quinones or carbonyls) and that adsorption of a non-polar organic (e.g., propane) is hindered by their presence on the surface. This is consistent with the well known immiscibility of polar and non-polar solvents, e.g., oil and water. The magnitude of the desorption energy suggests that the interaction between propane and the clean HOPG surface is greater than the interaction between propane molecules. There is no evidence of bilayer or multilayer formation under the present experimental conditions, because ambient pressure in excess of 10^{-6} Torr is necessary for propane bilayer formation at 90 K [39]. The propane adsorption capacity increase of air-cleaved HOPG after high temperature heat treatment is highly reproducible from sample to sample. During thermal treatment to 1050 K of air-cleaved HOPG from Advanced Ceramics, the desorption of gases containing 16, 18, 28 and 44 amu fragments was also observed in similar temperature regions to those evolved from SPI HOPG. TPD experiments using air-cleaved HOPG from Advanced Ceramics also verify that HOPG has almost no propane adsorption capacity after 473 K heat treatment and that its ability to adsorb propane increased by over an order of magnitude after heat treatment to 1050 K.

Interestingly, qualitatively similar behavior was reported in the study of xenon adsorption in carbon nanotubes

[40–42]. Thermal treatment above 600 K leads to desorption of oxygen- and hydrogen-containing functional groups, which are believed to block the entry ports of the nanotubes without changing the basic tubular structure of the nanotubes. The removal of these functional groups enhances the capacity of carbon nanotubes for xenon adsorption as well as the uptake efficiency (sticking coefficient) [40].

3.2. Plasma-oxidized HOPG

An important objective of our study was to understand the role of chemical and topological heterogeneity on adsorption and desorption on carbonaceous surfaces. In order to introduce defect sites and etch pits on HOPG, an air-cleaved HOPG sample was subjected to plasma treatment at controlled oxygen pressure. It has been shown previously that high temperature oxidation in air creates low density (<1% by surface area) of monolayer deep etch pits at existing defects of HOPG, while maintaining the flatness of the graphite surface [43–47]. Plasma oxidation, however, creates mechanical damage on initially flat surface that augments pre-existing defect sites [46]; it etches the surface, resulting in highly roughened surfaces confirmed by AFM measurements [46]. Images of plasma-oxidized HOPG acquired in air before mounting the samples in the UHV chamber are shown in Fig. 5. A significant density of defects (dark spots in Fig. 5b) is observed on the p-HOPG surface. The defects vary from ~10 to ~200 nm in diameter, and from ~1 to ~10 nm in depth. Plasma oxidation clearly results in the formation of a morphologically heterogeneous surface distinct from the topologically homogeneous air-cleaved surface. The a-

HOPG (Fig. 5a) shows a clean and flat surface except for a single step of ~2.5 nm height.

Similar features to those shown in Fig. 2 evolve during the heat treatment of plasma-oxidized HOPG. Exposure of plasma-oxidized HOPG to air for about 24 h results in essentially complete recovery of these features. This suggests that the oxygen-containing groups do not result from impurities incorporated during sample preparation or manufacture.

The effects of surface morphology on adsorption are depicted in Fig. 6, which compares TPD spectra from air-cleaved and plasma-treated HOPG at low propane exposure (<3 L) after heat treatment at 1173 K. TPD spectra for air-cleaved HOPG below 3 L propane exposure consist of a single peak with a leading common edge. On the other hand, for plasma-oxidized HOPG, it consists of two peaks, at around 120 and 175 K, which both grow together with propane exposure. The growth of the lower temperature peak with exposure resembles that observed for the air-cleaved HOPG except that the peak height is an order of magnitude lower. The higher temperature peak shifts to lower temperatures with increasing exposure. We believe that the TPD spectra observed on p-HOPG are a consequence of the defects generated by plasma treatment. These defects provide adsorption sites with stronger binding energy, as indicated by the high temperature peak. The downward shift in peak temperature with increasing exposure suggests sequential filling of the defect sites, with the higher binding energy sites being filled first. This behavior also suggests significant mobility of adsorbed species enabling them to sample all the sites. In addition, the TPD areas for plasma-oxidized HOPG are always greater than those for the air-cleaved HOPG under identical exposure

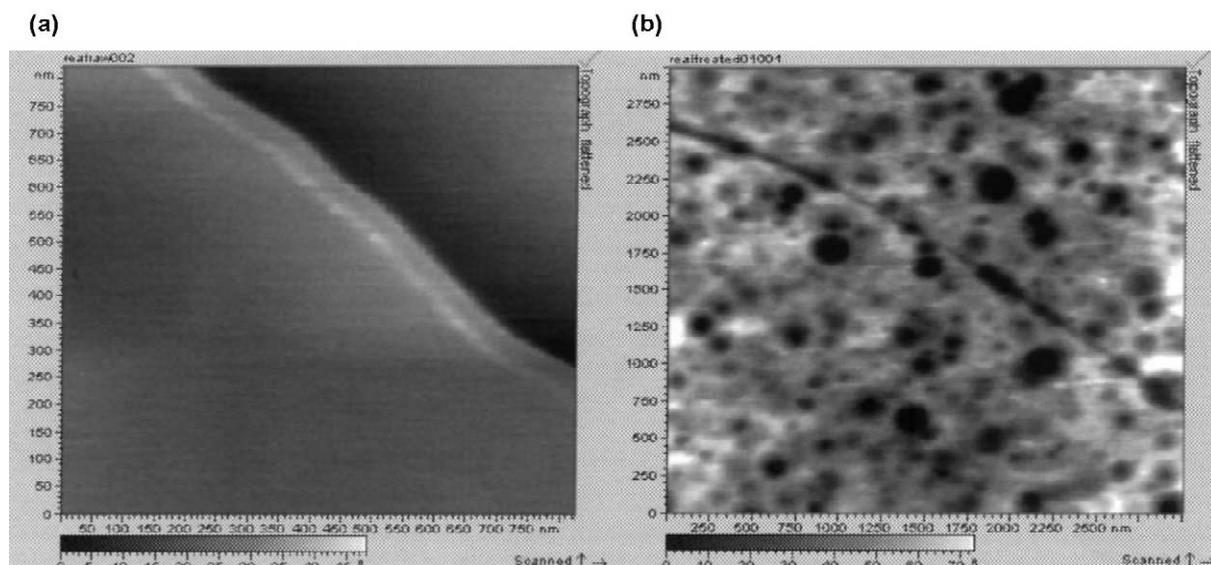


Fig. 5. AFM images for (a) air-cleaved and (b) O₂ plasma-oxidized HOPG surface.

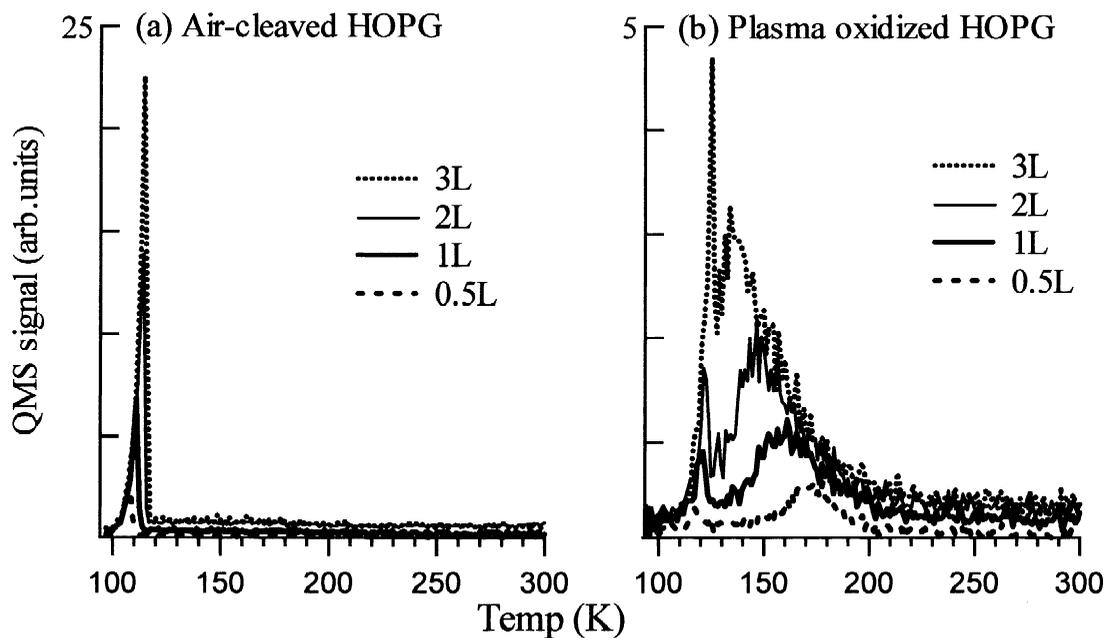


Fig. 6. TPD spectra after 1173 K substrate heat treatment for air-cleaved HOPG (a) and O_2 plasma-oxidized HOPG (b). The same arbitrary units are used in (a) and (b) to facilitate comparison.

conditions, as shown in Fig. 7. Hence, the capacity for propane adsorption on plasma-oxidized HOPG is greater than on air-cleaved HOPG. In addition, plasma-oxidized HOPG has pits that are several tens of layers deep, thereby providing access to many more graphite layers than air-cleaved HOPG. Control experiments with a gold-coated Ta sample indicate that the quantity of propane desorbed from a gold-coated Ta sample is similar to that desorbed from the heat-treated air-cleaved HOPG. These results suggest that no propane intercalation occurs under the experimental condition used in this study. Therefore, the observed increase in uptake capacity of plasma-oxidized HOPG of

about 50% is most likely associated with the increased surface area provided by the topologically heterogeneous plasma-oxidized HOPG sample [40].

4. Conclusions

Oxygen- and hydrogen-containing functional groups exist on both air-cleaved HOPG and plasma-oxidized HOPG. They can be removed by thermal treatment. The removal of those groups leads to an increase in adsorption capacity for a non-polar organic compound, propane, by more than one order of magnitude. It is essential for carbonaceous surfaces to be thermally treated above 1173 K, so that functionality, which only provides low energy adsorption sites for propane, can be removed. HOPG surfaces exposed to ambient air are most probably covered with such functional groups that affect their sorption properties. The surface defects induced by plasma oxidation of HOPG provide a higher surface area and topologically heterogeneous carbonaceous surface. These defects also provide higher energy adsorption sites.

By studying a pore-free carbon, i.e., air-cleaved HOPG, we can attempt to separate chemical and topological heterogeneity. Chemical functionality alone can hinder the adsorption of simple molecules. This study provides insight into the role of chemical and topological heterogeneity in the adsorption process on carbonaceous surfaces that are commonly used in technological applications.

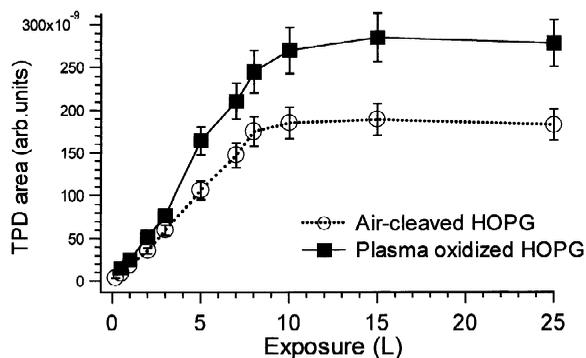


Fig. 7. TPD area as a function of propane exposure for both air-cleaved and plasma-oxidized HOPG after 1173 K substrate heat treatment.

Acknowledgements

This work is supported by the US Department of Energy under grant No. DE-FG26-98FT40119. We acknowledge Dr. Yufan He for help in obtaining the AFM images, and Dr. William R. Wagner and Mr. Brian Fill for assistance in plasma oxidation treatment of HOPG. We thank Professor J.T. Yates, Jr. for the loan of the propane gas.

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