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Characterization of the surface carbonyl and hydroxyl coverage on glassy carbon electrodes using Raman spectroscopy

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Abstract

A fluorescein derivative was synthesized and covalently bonded to hydroxyl groups on glassy carbon surfaces. Since the fluorescein fluorescence was quenched by the carbon surface, its resonance Raman spectrum could be observed at surface coverages of approximately 1%. The fluorescein/GC bond was stable to repeated sonication in ethanol, but was rapidly hydrolyzed by mild base. This new label for surface hydroxyl groups was combined with a similar label for carbonyl groups to assess changes in the coverage of surface C–OH and C=O with GC pretreatment. The relative densities of these species varied with both the initial GC heat treatment and with subsequent chemical treatment in hot HNO_3 or hot KOH solutions. HNO_3 increased the C=O coverage on vacuum heat treated (VHT) GC, while KOH increased the C–OH coverage. Chemical treatments of GC following polishing or heat treatment were less selective, due to the significant initial coverage of C=O and C–OH. In all cases, significant surface oxygen on GC was present in forms other than C=O and C–OH.

Keywords: Raman spectroscopy; Glassy carbon electrodes; Hydroxyl groups; Carbonyl groups

1. Introduction

The importance of oxygen containing functional groups to carbon electrode surface chemistry has been documented extensively, particularly with respect to electrochemical processes [1–7]. Surface oxides form spontaneously on most carbon surfaces in air, and are unavoidable without special effort, such as UHV heat treatment [8–10]. Of particular relevance to the present work is the association of surface oxides with electron transfer catalysis, by redox mediation or other interactions with solution phase redox centers [1,9,11–13]. For example, the presence of surface carbonyl groups can increase the heterogeneous electron transfer rate for the $Eu_{aq}^{+3/+2}$ system at glassy carbon (GC) by a factor of 100 [14]. Although the importance of particular surface oxides to electrode kinetics at carbon electrodes is well recognized, their surface coverage is hard to control. The type of carbon material, its pretreatment, exposure to air or electrolyte, and potential excursions can all affect the total oxide coverage as well as the distribution of oxide types (phenolic, carbonyl, carboxylate, etc.) on a particular carbon surface. A variety of surface preparation procedures and analytical techniques have been investigated, which lead to a wide range of surface structures and oxide coverages.

XPS has been used extensively to characterize oxides on carbon, most commonly by deconvolution of the C_{1s} and O_{1s} peaks in high resolution spectra [12,15–24]. Sherwood and coworkers have examined a variety of surface treatments of carbon fibers, and determined surface coverage of alcohol/ether groups, carbonyl groups, and carboxylates [15–21]. Total oxide coverage was as high as 50%, but generally 10–15%, with the principal species being alcoholic (3–7% coverage) and carbonyl (3–5%) groups. Cabaniss, et al. reported 15% coverage of alcohol/ether groups and 5% of C=O for polished GC, and 21 and 9% after electrochemical activation [12], while Kamau et al. [25] reported 7% C=O coverage for polished GC. Tougas and Collier [26,27] developed chemically specific labels for surface OH and C=O groups which yielded XPS tags observable without deconvolution. They reported carbonyl coverages of 1.5–2.0% [26] and phenolic coverage of

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1–10% [27] for polished GC. Kuwana et al. monitored oxide coverage of carbon surfaces exposed to oxygen, water, and NH_3 plasmas, and introduced ultrahigh vacuum heat treatment for GC [6,8,28,29].

Vibrational spectroscopy differs fundamentally from XPS in that it provides information about molecular structure rather than elemental composition. FTIR has been applied to studying oxides on carbon for high surface area materials or for thick films, but is not yet capable of submonolayer sensitivity on electrode surfaces [2,30–34]. Raman spectroscopy has the added feature of providing information about the carbon substrate as well as the adsorbate, and several examples of monolayer sensitivity have been reported. Unenhanced adsorbates yielded useful Raman spectra for monolayer coverage on GC and graphite [35,36], while resonance enhancement permitted submonolayer detection limits and the determination of adsorbate orientation [37–39]. Of particular relevance to the current work is the labeling of surface C=O groups with dinitrophenyl hydrazine (DNPH), yielding a resonance enhanced DNPH adduct [39–41]. This reaction was chemically specific for surface C=O groups, and permitted C=O coverage to be assessed at levels in the 1–10% range. Fluorescent labels of surface oxides have also been developed, in order to provide a spatially resolved probe of functional groups on carbon fibers [42–44].

The current work had two main objectives. First, a resonance Raman active label for surface C–OH groups was sought, in order to assess C–OH coverage with good selectivity. Second, the effects of pretreatments of GC surfaces on surface C–OH and C=O densities were examined, using two different resonance Raman labels. The long range goal is control and evaluation of surface functional group populations.

2. Experimental

2.1. Reagents and materials

Glassy carbon (GC-20) was purchased from Tokai (Japan) as a single $100 \times 100 \times 3$ mm^3 plate. The plate was cut into smaller $1 \times 1 \times 0.3$ cm^3 pieces for convenient handling and sample preparation. In all cases the GC pieces were initially cleaned by dry sanding first with 180 grit Carbimet (Buehler) then 600 grit Carbimet, followed by sonication in 18 MΩ cm Nanopure (Barnstead) water. The carbon was then polished using 1.0, 0.3, and 0.05 μm alumina in Nanopure water slurries, with sonication in Nanopure water for 10 min following the final 0.05 μm polish. The freshly polished carbon samples were dried using argon before undergoing further pretreatment. A 10 mM solution of 2,4–dinitrophylhydrazine (J.T. Baker) was prepared using dry ethanol (Aaper) containing 1% HCl (J.T. Baker). Reagents for the synthesis of the fluorescein mixed anhydride (FMA) were used as purchased including triethylamine and ethyl chloroformate from Fisher Scientific and fluorescein from Aldrich. Dinitrobenzoylchloride, dimethyl amino pyridine, 9-fluorenone, and naphthol were also used as purchased from Aldrich. Dichloromethane from Mallinckrodt was dried by passing through a column of basic alumina (Fisher) before use in FMA synthesis. 70% nitric acid from Fisher was used as received in the nitric acid bath experiments. 10 M KOH (J.T. Baker) was prepared in Nanopure water for KOH bath experiments.

2.2. Instrumentation

Raman spectra were acquired using 514.5 nm excitation from a Coherent Innova 90 Ar^+ laser with the spontaneous emission blocked by a 514.5 nm dielectric band pass filter. The spectrograph was a 250 mm focal length $f/4$ imaging spectrograph from Chromex (Albuquerque, NM). The entrance slit to the spectrograph was opened to 100 μm, and the grating had 1800 lines mm^{-1} blazed for the visible region of the spectrum. The Rayleigh scattered photons were rejected using a 1 mm thick single crystal of CdS (Cleveland Crystals) placed just before the entrance slit to the spectrograph. The collection and focusing optics were configured as described elsewhere [36] except that a cylindrical lens was placed between the laser and the steering mirror to produce a line focus at the sample. The line focus was oriented parallel to the entrance slit, and reduced the laser power density at the sample. Laser power at the sample was 50 mW, distributed over an approximately 100×2000 μm^2 focus. A Photometrics 1152×296 front-illuminated CCD was used as the detector, and was held at -110°C to reduce the dark signal. Three integrations of 120 seconds each were averaged to obtain surface spectra. The carbon substrate spectrum was subtracted where noted.

2.3. XPS and vacuum heat treatment

XPS spectra were acquired using a VG Scientific ESCALAB MKII spectrometer with a Mg X-ray source. Samples that were vacuum heat-treated (VHT) were placed on a molybedenum sample stub, containing a resistive heater (Kurt Lesker), which was then placed in the UHV chamber. The initial pressure of 10^{-9} Torr increased to 10^{-7} Torr for the first 15 min and then dropped to 10^{-8} for the remainder of the heating period. The samples were heated by passing a current of 2.8 A, which corresponds to a stub temperature of 650–700°C, for 2 h.

Heat treatment under 0.99999 N_2 atmosphere was carried out using a Lindberg resistive tube furnace and Eurotherm controller. Freshly polished carbon samples

were placed in a quartz vessel with a slow flow of N_2. The quartz vessel was purged with N_2 for 10 min before the start of the heating cycle. Samples were then heated to 575°C in 6 min, then held at 575°C. After 5 h at 575°C the carbon samples were removed while still hot from the quartz vessel and immediately placed into solution for derivatization or chemical pretreatment.

2.4. Fluorescein mixed anhydride synthesis

In a N_2 purged three neck round bottom flask, 5.0 g of fluorescein were added to 250 ml of dry dichloromethane. To the stirred fluorescein + dichloromethane solution, 2.9 g of triethylamine were added. Using an addition funnel, 2.72 ml of ethyl chloroformate was added to the reaction over a period of 30 min. The reaction was kept at 0°C using an ice bath around the round bottom flask. Initially, the fluorescein was only slightly soluble in the dichloromethane, and a large amount of solid remained at the bottom of the flask. However, the FMA product was very soluble in the dichloromethane, and therefore provided a convenient means to monitor the progress of the reaction. After 2 h, the supernatant was decanted from any insoluble fluorescein that remained. The supernatant was rotary-evaporated to produce a slightly waxy orange solid. The product was further dried using a mechanical vacuum pump overnight. NMR and mass spectrometry results are consistent with the desired FMA product, shown in Fig. 1.

2.5. Surface oxide derivatization procedures

Surface carbonyl groups were derivatized using the procedure of Fryling et al. [40]. The carbon sample was placed in 25 ml of 10 mM DNPH solution in absolute ethanol containing 1% HCl. The carbon and solution were heated to 75°C, and then the heat was removed from the reaction and the solution allowed to cool. After 2 h of total reaction time the carbon was removed from the DNPH solution, quickly rinsed in absolute ethanol, and then soaked for 15 min in a solution of absolute ethanol with 0.1 M KOH. The carbon was removed and rinsed a final time in absolute ethanol and dried with ultrapure argon before being analyzed with Raman spectroscopy. The Raman spectrum of DNPH derivatized carbon has several features, which have been characterized previously [40]. The 830 and 925 cm^{-1} bands are used here due to the relatively flat baseline in this region and the lack of interference from the GC-20 bands.

Two different surface probes were used to derivatize the surface hydroxyl groups. The first method was originally reported by Chen et al. [14], and the same conditions were used. The carbon sample was reacted with dinitrobenzoylchloride in pyridine, forming an ester bond to surface hydroxyls. After the reaction was completed, the carbon was rinsed in copious amounts of pyridine to remove physisorbed DNBC. The carbon was then sonicated in water for ten minutes and dried in argon, before being mounted with conductive carbon tape on an XPS sample stub. The carbon sample was then introduced into the XPS system, where both survey and high-resolution spectra were acquired. The surface bound DNBC gives a unique NO_2 signal at 406 eV. The amount of surface hydroxyl groups was estimated from the NO_2/C ratio on the DNBC derivatized surface.

The second method for characterizing the surface hydroxyl groups involved using the resonance Raman probe molecule FMA. The carbon sample to be derivatized was rinsed with dry dichloromethane before being placed in 40 ml of 15 mM FMA in dry dichloromethane. The FMA + carbon solution was vigorously stirred during the addition of 58 mg of triethylamine and 2.5 mg of DMAP. The reaction solution was stirred for 36 h at which time the carbon was removed and rinsed with dichloromethane. In order to ensure that physisorbed FMA was removed from the carbon surface a vigorous rinsing sequence was applied. First the carbon was placed in an absolute ethanol solution and stirred for an hour, with the ethanol solution being changed once during this time. The carbon was then sonicated in fresh ethanol for 10 min,

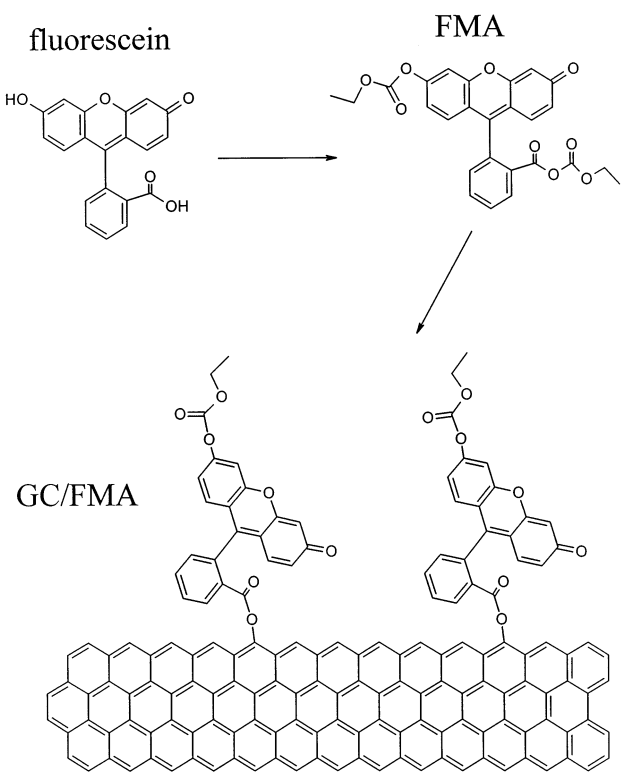

Fig. 1. Structure of fluorescein mixed anhydride (FMA) reagent, and the probable product of a reaction with surface C–OH groups.

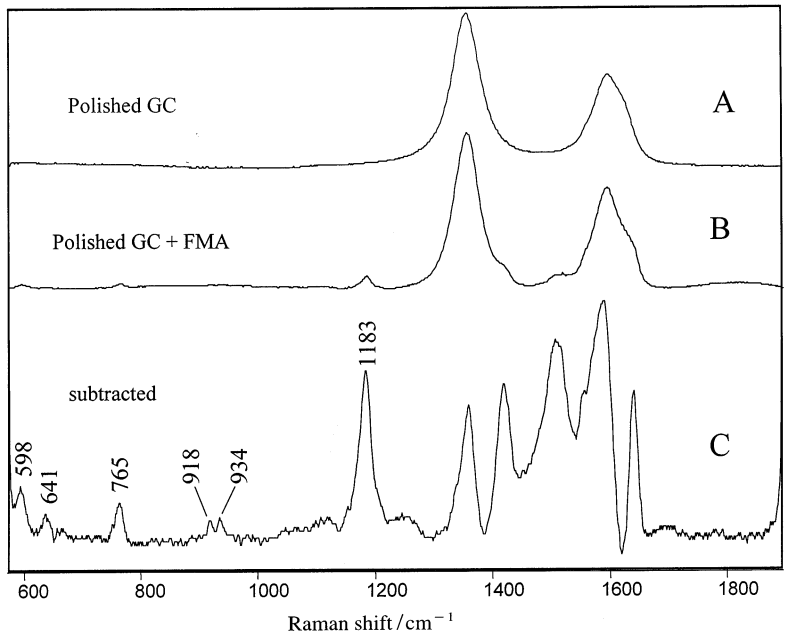

Fig. 2. Raman spectra of polished GC before and after FMA derivatization, spectrum A is GC before derivatization; B is after FMA treatment and sonication in ethanol. Spectrum C is the difference of B–A, after normalization of the 1360 cm^{-1} carbon bands to the same height.

and dried under argon gas. Raman spectra were acquired from at least three different spots on the surface, with the average peak area ratio of the 765 cm^{-1} band versus the 1360 cm^{-1} band being used to determine the surface hydroxyl concentration.

2.6. Chemical pretreatment procedures

In order to modify the distribution of surface oxides, polished and heat treated GC samples were exposed to hot HNO_3 or hot KOH. After VHT or N_2 heat treatment as described above, samples were either exposed to 70% nitric acid at 115°C or 10 M KOH at 100°C for 1 h, then sonicated in Nanopure water for 15 to 20 min. After sonication, the samples were immediately derivatized or subjected to XPS analysis.

3. Results and discussion

The first issue considered was the specificity and sensitivity of the newly synthesized FMA probe molecule towards –OH functionalities. From classical organic chemistry, an acid anhydride should form a covalent ester bond with alcohols, but not with aldehydes, ketones, or carboxylic acids. Fig. 1 shows the expected reaction of FMA with a surface hydroxyl group on GC. FMA was tested for reactivity with aromatic hydroxyls by conducting the FMA derivatization with naphthol and 9-fluorenone. Raman spectroscopy could not be used to characterize the products because of the fluorescein luminescence in solution, but the reactions could be monitored with TLC and FTIR. No products were detected after 48 h of reaction between FMA and 9-fluorenone, but the FMA/naphthol reaction did yield a new TLC spot. FTIR of this product showed the expected ester linkage for a naphthol-FMA adduct. Comparison of the observed FTIR frequencies with those calculated with Gaussian 94 using a 3-21G basis set showed good agreement [45].

Fig. 2 shows Raman spectra of polished GC before and after FMA derivatization. The resonance enhanced cross section of fluorescein combined with fluorescence quenching by the carbon surface leads to relatively easily observed surface bands for the FMA bound to surface –OH groups. Spectra of physisorbed FMA were obtained by exposing the polished GC to a solution of FMA in CH_2Cl_2 followed by a brief rinse. Surface Raman spectra for chemisorbed and physisorbed FMA do not differ greatly, since most of the scattering originates in the fluorescein nucleus common to both. Physi- and chemisorbed FMA have similar Raman features at 464–466, 598, 641, 765, 918, 932 and 1183 cm^{-1}, plus some features partially obscured by the carbon phonons at 1360 and 1590 cm^{-1}. There are some FMA Raman features in the region from 1300–1650 cm^{-1}, but these are considered unreliable for quantitative purposes due to the difficulty of accurate subtraction of the relatively strong 1360 and 1590 cm^{-1} carbon phonons. Note that the 765 cm^{-1} band of the chemisorbed spectrum of Fig. 3(B) is used in subsequent quantitative evaluation of –OH coverage. To verify that the spectra of Figs. 2(B and C) were not from physisorbed FMA, the chemisorbed surface was

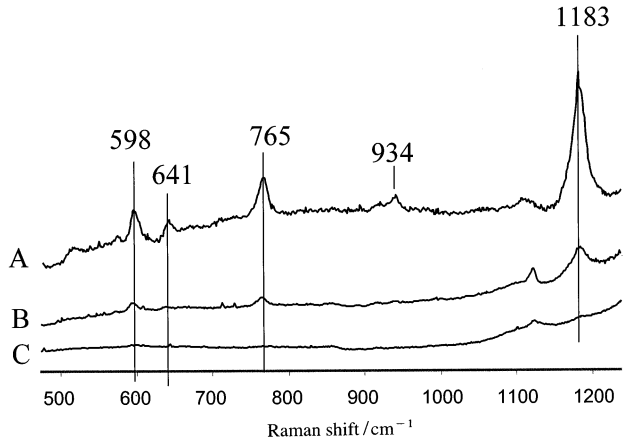

Fig. 3. Effect of ethanol and 0.1 M KOH on surface spectra of derivatized GC. Spectrum A is immediately after FMA derivatization and a brief EtOH rinse. Spectrum B is after 30 min of sonication in EtOH, and Spectrum C is after 20 min of sonication in 0.1 M KOH. Substrate spectra were not subtracted.

sonicated repeatedly in ethanol, followed by reaction with 0.1 M KOH. Spectra are shown in Fig. 3 for the GC surface following derivatization, after sonication in ethanol, and after KOH treatment. The area ratio of the 765 cm^{-1} FMA band to the 1360 cm^{-1} carbon band is listed for various treatments in Table 1. Sonication in absolute ethanol following the FMA reaction removes a significant fraction of the surface FMA signal, presumably by removing physisorbed reagent. After the initial rinse, however, further sonication in ethanol has a minor effect. Sonication in 0.1 M KOH, which should hydrolyze the FMA/surface ester bond, causes a precipitous drop in the 765 cm^{-1} band. These results indicate that FMA chemisorbs to the GC surface via a linkage which is hydrolyzable by 0.1 M KOH. As noted in the experimental section, all FMA derivatizations were followed by a 1 h soak in ethanol and a 10 min sonication in fresh ethanol to remove physisorbed FMA.

The reactivity of FMA with surface –OH groups on GC was compared to a previous derivatization reagent, dinitrobenzoyl chloride (DNBC). DNBC provides an XPS marker for surface –OH via its nitro groups [14],

Table 1
Effect of solvent washes on surface Raman intensity

Polished GC	765/1360 band area ratio
After FMA derivatization	0.0078
After 30 min sonication in ethanol	0.0021
After additional 30 min sonication in ethanol	0.0018
After additional 30 min sonication in ethanol	0.0018
After 20 min sonication in 0.1 M KOH	0.0003

Table 2
Comparison of changes in surface hydroxyl coverage assessed by Raman and XPS

Pretreatment [a]	765/1360 peak area ratio after FMA	XPS N/C ratio after DNBC
N_2, 575°C	0.0079	0.009
N_2, 575°C plus 100°C KOH in water	0.023	0.029
N_2, 575°C plus 115°C HNO_3 in water	0.0070	0.006

[a] All GC samples were polished initially in $Al_2O_3 + H_2O$.

but cannot be detected with Raman techniques using current technology. Table 2 compares the effects of three pretreatments on the surface –OH coverage of GC, assessed by both Raman after the FMA reaction and by XPS after the DNBC reaction. Separate samples of polished GC were pretreated identically before FMA or DNBC derivatization. The surface –OH concentrations assessed by these two methods show similar qualitative and quantitative trends, with pretreatment in hot KOH solution causing a significant increase in –OH coverage. The correlation of the 765 cm^{-1} FMA Raman band with the N/C ratio for DNBC lends confidence to the specificity of FMA for surface OH groups.

Once Raman labels for surface C=O and C–OH were in hand, a variety of GC pretreatments were examined to assess their effects on –OH and C=O density. Twenty-seven GC-20 samples were polished in an identical fashion in an $Al_2O_3 + H_2O$ slurry, then divided into nine groups of three samples. Each group was pretreated by vacuum heat treatment (VHT) or heating to 575°C in 99.999% N_2, and in some cases by exposure to hot HNO_3 or KOH solutions. Samples from each group were then analyzed by XPS to obtain the total O/C ratio, by FMA derivatization and Raman spectroscopy to assess surface –OH, and DNPH followed by Raman spectroscopy to assess surface C=O. Representative Raman spectra are shown in Fig. 4, for the VHT sample followed by HNO_3 or KOH treatment before DNPH or FMA derivatization. Distinct Raman features for the FMA/OH adduct are apparent, particularly the 765 cm^{-1} band. The 765/1360 cm^{-1} peak area ratio indicates relative –OH coverage, as noted earlier. The 925/1360 cm^{-1} peak area ratio from the DNPH/C=O adduct was used similarly to assess relative C=O coverage. Semiquantitative trends are apparent from Fig. 4, with HNO_3 causing increases in both surface C=O and C–OH densities, but with a larger increase for C=O. In contrast, KOH causes an increase in surface C–OH, with little effect on surface C=O.

Examination of the quantitative results in Table 3 reveals that the densities of –OH and C=O depend not only on the chemical pretreatment, but also on the initial conditions. For example, the effect of HNO_3

exposure depends on the initial density of C=O, which in turn depends on whether the initial surface was polished or heat treated. The simplest case is the initially vacuum heat treated samples, lines 1, 4, and 5 in Table 3. The VHT surface has the lowest O/C ratio, and therefore the lowest initial C–OH and C=O densities. Treatment of a VHT surface with hot KOH (line 4) increases the C–OH density by a factor of about 3, while it decreases C=O by 22%. Conversely, treatment of the VHT surface with hot HNO_3 increases C=O by a factor of 13, but increases surface –OH by only 63%. Notice that conventional polishing (line 2) leads to nonselective increases in surface C–OH and C=O compared to the VHT surface. At least for the case of the VHT surface, the KOH and HNO_3 treatments yield selective increases in surface C–OH and C=O, respectively.

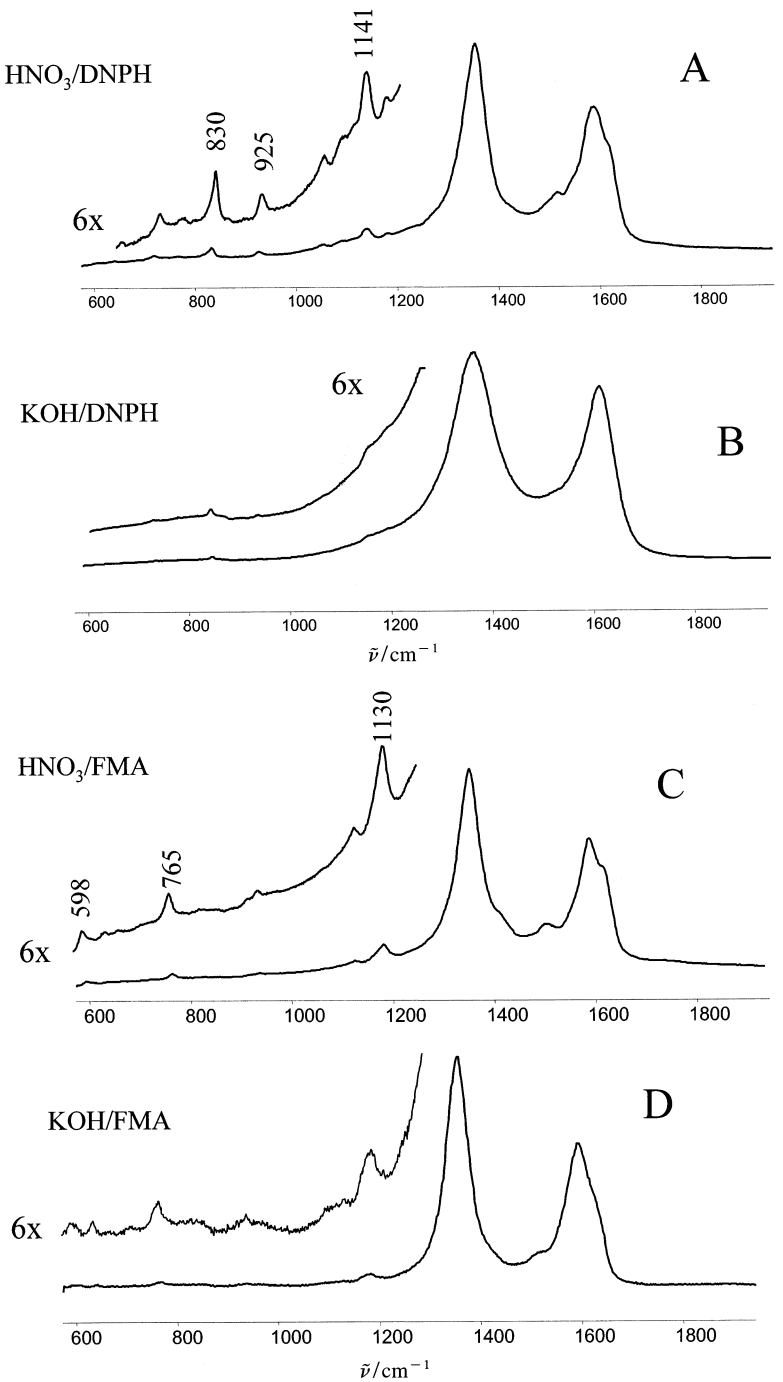

Fig. 4. Raman spectra of GC following vacuum heat treatment, exposure to hot HNO_3 (A and C) or hot KOH (B and D) and derivatization with DNPH (A and B) or FMA (C and D). Carbon substrate spectra were not subtracted.

Table 3
Effects of surface treatments on surface oxide Raman and XPS features

Treatment [a]	XPS O/C	DNPH 925/1360 peak area ratio	DNPH area ratio relative to VHT	FMA 765/1360 peak area ratio	FMA area ratio relative to VHT
VHT	0.04	0.0006	1.000	0.0019	1.000
None	0.14	0.0063	10.4 ± 2.5 [b]	0.0055	2.90 ± 0.7 [b]
N_2 (575°C)	0.12	0.0064	10.6 ± 0.9	0.0079	4.12 ± 1.2
VHT + KOH	0.23	0.0005	0.78 ± 0.09	0.0055	2.90 ± 0.7
VHT + HNO_3	0.29	0.0083	13.7 ± 1.6	0.0031	1.63 ± 0.06
KOH	0.10	0.0035	5.8 ± 0.09	0.0053	2.76 ± 0.7
HNO_3	0.19	0.0114	18.9 ± 1.6	0.0072	3.74 ± 0.8
N_2 (575°C) + KOH	0.11	0.0140	23.1 ± 6.9	0.0232	12.1 ± 2.7
N_2 (575°C) + HNO_3	0.19	0.0073	12.1 ± 3.5	0.0070	3.64 ± 0.8

[a] All surfaces initially polished with $Al_2O_3 + H_2O$ slurry.
[b] Mean ± standard deviation, for three repetitions.

The effects of KOH and HNO_3 on the polished or N_2 surfaces are less obvious, mainly because these surfaces have significant C–OH and C=O density before exposure to KOH or HNO_3. Comparison of lines 8 and 3 in Table 3 indicates that KOH significantly increases C–OH coverage, but also increases C=O to a lesser degree. For the polished GC (lines 2, 6, 7), HNO_3 increases C=O while KOH decreases C=O, while the effects on surface C–OH are relatively minor. Overall, it is clear that attempts to enrich C=O or C–OH selectively succeed or fail depending on the initial surface. As a more quantitative indication of selectivity, we may define a selectivity ratio as the ratio of the normalized DNPH peak area ratio (5th column in Table 3) to the normalized FMA ratio (7th column), using the VHT surface as a reference. If a procedure increases C=O compared to C–OH, this selectivity ratio is greater than 1, while selective increase of C–OH yields a ratio less than 1. Selectivity ratios for several starting points are listed in Table 4. Although HNO_3 leads to selective increases for C=O compared to C–OH in most cases, the selectivity is most pronounced for the VHT surface.

A variety of reports on modifying C=O and C–OH coverage have appeared previously, based mainly on XPS results [15–29]. Given the dependence on initial conditions observed in the present work, it is not surprising that significant variability occurs in reported C–OH and C=O values. Several mechanistic effects may contribute to this variability. Oxide formation on carbon surfaces is generally irreversible, and oxides are difficult to remove, once formed. So HNO_3 has minor effects on existing surface C–OH even though it may increase C=O. There may be a limited number of carbon sites amenable to oxide formation, making it difficult to add oxides to an already oxidized surface. Thus a surface with $> 10\%$ O/C ratio is less prone to modification than one with low O/C ratio. The irreversibility of oxide formation accounts for the high selectivity observed for HNO_3 and KOH treatment of the VHT surface. Since the VHT surface is low in C=O and C–OH but presumably rich in potential oxidation sites, the HNO_3 and KOH reactions can proceed more selectively. The nitrogen heat treatment did not reduce the oxide level to the low values observed for VHT, either because of residual oxygen in the N_2 gas, or because of oxidation of the hot surface during brief (< 1 s) exposure to air before derivatization.

The peak area ratios in Table 3 are not calibrated in terms of quantitative C–OH or C=O coverage, but their relative values indicate changes and trends. Comparison to the DNBC XPS results (Table 2) reveals that the range of 765/1360 area ratios listed in Table 3 (column 6) correspond to approximately 0.2–2% of the surface carbon atoms having OH groups. Fryling et al. reported C=O coverage of polished surfaces of approximately 1% [40]. These values are consistent with the 1–5% coverages reported by Tougas, et al. [26] based on XPS of chemically labeled C=O groups on GC. Collier and Tougas also reported a range of surface OH groups of 1–10% based on XPS of titanium labeled GC surfaces [27], with three of four surfaces studied having a range of 1.2–4.5%. Notice that C–OH and C=O coverages from both XPS and Raman labels of a few percent do not account for the 12–29% O/C ratios listed in Table 3. The significant shortfall could be due to ether, carboxylate, or lactone oxygen atoms which

Table 4
Selectivity ratios for C=O/C–OH [a]

Surface	Initial	After HNO_3	After KOH
VHT	1.00	8.3	0.27
Polished	3.6	5.1	2.1
N_2 (575°C)	2.6	3.3	1.9

[a] Ratio of 925 to 765 cm^{-1} peak area, relative to that for a VHT surface.

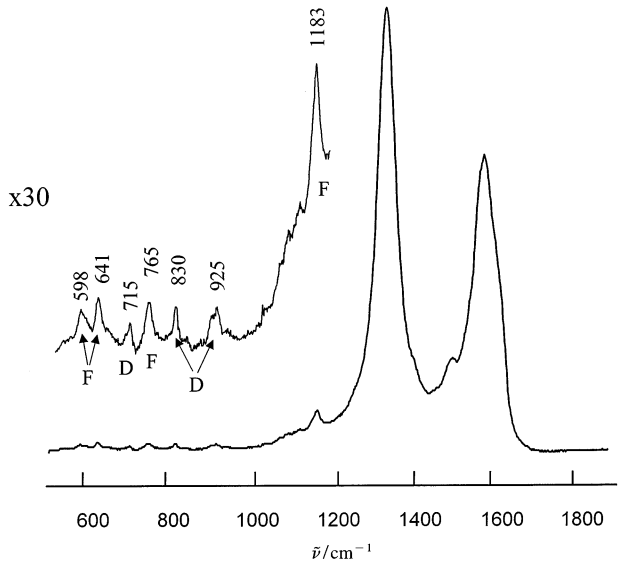

Fig. 5. Raman spectrum of polished GC derivatized with both FMA and DNPH reagents. 'D' and 'F' indicate bands attributable to modified C=O and C–OH groups, respectively. Substrate spectrum not subtracted.

do not react with FMA or DNPH. Whatever their nature, a significant fraction of surface oxygen is not identified as hydroxyl or carbonyl.

The hydroxyl and carbonyl densities reported here are also lower than those based on deconvolution of the C_{1s} peak of high resolution XPS. An XPS chemical shift is not as selective as Raman, however, and may overstate the C–OH coverage. Phenolic or ether C–O linkages will yield similar shifts in C_{1s} binding energy. Raman is very selective for molecular structure, and thus for specific functional groups, provided the derivatization reaction is itself selective. To illustrate, Fig. 5 shows GC modified with both FMA and DNPH, showing distinct peak frequencies attributable to each derivatizing agent. An alternative explanation for the low C–OH and C=O coverage observed by Raman is the possibility of incomplete derivatization, possibly due to steric hindrance of the large FMA molecule. The low coverages observed with the FMA label are consistent with results from XPS labels [26,27], even though the labels used for XPS are much smaller molecules. If the FMA label does yield a low estimate of hydroxyl coverage due to incomplete derivatization, the trends observed with various electrode pretreatments would still be valid.

Although based on different phenomena, the Raman labels used here have the same objective as fluorescent tags used to identify surface functional groups on carbon fibers [42–44]. Both techniques are amenable to microscopy, permitting spatially resolved measurements of functional group density [39,42]. In the absence of quenching, fluorescence is more sensitive than Raman, and involves less expensive equipment. However, fluorescence is quenched on GC unless the label is a significant distance from the surface. In addition, the greater resolution and structural information available from Raman permits the use of multiple labels, as in Fig. 5.

In summary, the FMA is a specific and surface sensitive resonance Raman probe for hydroxyl groups at the surface of GC-20 electrodes. The surface oxide distribution is sensitive to both the initial conditions and subsequent chemical treatment procedures. Selective enrichment of surface hydroxyls was observed for KOH treatment of a vacuum heat treated surface, while surface C=O was selectively enriched by hot HNO_3. The use of resonance Raman probes has the potential to detect phenolic and carbonyl functional groups on the same surface simultaneously.

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