Monitoring desorption of adsorbed water on a hydrophilic layer on an amorphous carbon surface by PM-IRRAS

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Keywords

- Adsorption/desorption kinetics
- Biosensing applications
- PEM
- Photoelastic modulation
- PM-IRRAS

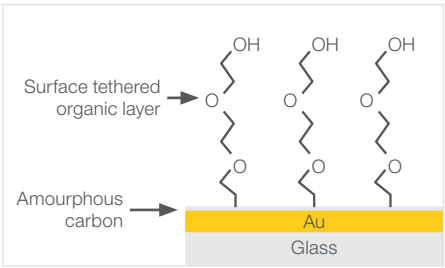

Figure 1. Idealized schematic of di(ethylene glycol) ether modified surface.

Figure 2. PEM module and GWC SSD100 demodulator (right).

Introduction

Organically modified amorphous carbon substrates are thought to be an excellent alternative to glass or gold substrates for applications such as MEMS and DNA array sensors. Amorphous carbon-tethered films are more stable at elevated temperature and extended exposure to solution media.[1-2]

In this study, desorption of environmental moisture on a di(ethylene glycol) vinyl ether (CH_2=CH($OCH_2CH_2)_2$OH) modified amorphous carbon surface (Figure 1) is monitored by polarization modulation infrared reflectance absorption spectroscopy (PM-IRRAS). The EG2-modified carbon surface is hydrophilic and provides a surface that strongly resists protein adsorption and is potentially useful for biosensor applications.

PM-IRRAS using photoelastic modulation (PEM) combined with real-time processing electronics effectively allows analysis of very thin layers of surface species without interferences from isotropic gas phase species. The change in the amount of adsorbed moisture on this hydrophilic surface is monitored over time. General IRRAS surface selection rule applies here; hence, changes in molecular orientation can be probed.

Experimental details

Sample: Di(ethylene glycol) vinyl ether (EG2) was tethered to amorphous carbon surface via an ultraviolet photochemical reaction, as described by Hamers et al.[1] The thickness or uniformity of the film was not evaluated, however it is assumed to be a multilayer film.

Instrumentation: Data was acquired using the Thermo Scientific™ Nicolet™ 8700 Spectrometer with a PEM module equipped with a liquid nitrogen cooled MCT detector (Figure 2). Additionally, an SSD100 demodulator (GWC Technologies, Madison, Wisconsin, USA) was used for real-time demodulation of signal. The Nicolet 8700 spectrometer has been discontinued, but the current range of Thermo Scientific™ FTIR spectrometers can provide similar measurements and performance. The sample was analyzed at 82° incidence angle. The sample compartment was N_2(g) purged. Prior to the analysis, the sample was kept in an ambient laboratory environment. First, a spectrum was collected with the sample compartment open. The sample compartment was then closed and spectra were collected sequentially. After 24 hours, the sample compartment was opened again, and the data collection was repeated.

Results

EG2-modified amorphous carbon sample surface is hydrophilic. Water readily adsorbs from the atmosphere as evidenced by an increase in the ν(OH) band of water immediately after the opening of the sample compartment.

Water ν(OH) and δ(OH) bands at ~3500 and 1640 cm^{-1}, respectively, show a decrease in intensity immediately after the sample compartment is closed (Figure 3a). The intensity decrease of the water vapor signal is also observed in the sum signal (Figure 3b).

Changes in the integrated area of liquid water ν(OH) band and intensity of gas phase water ν(OH) band are plotted against time in Figure 4a and b, respectively. Amounts of surface and gas phase water decrease with time, however, at a different rate. Gas phase water decreases relatively linearly whereas surface water rapidly desorbs at first and then the desorption rate slows down. This observation suggests that some of the water molecules at the surface are more strongly interacting with the EG2 surface through hydrogen bonding.

In addition to changes in amount of water on the surface, intensities of $\nu(CH_2)$ bands increase with a decrease in amount of water suggesting orientation change of methylene group. On average, methylene groups seem to increase its carbon chain tilt orienting itself more perpendicular to surface.

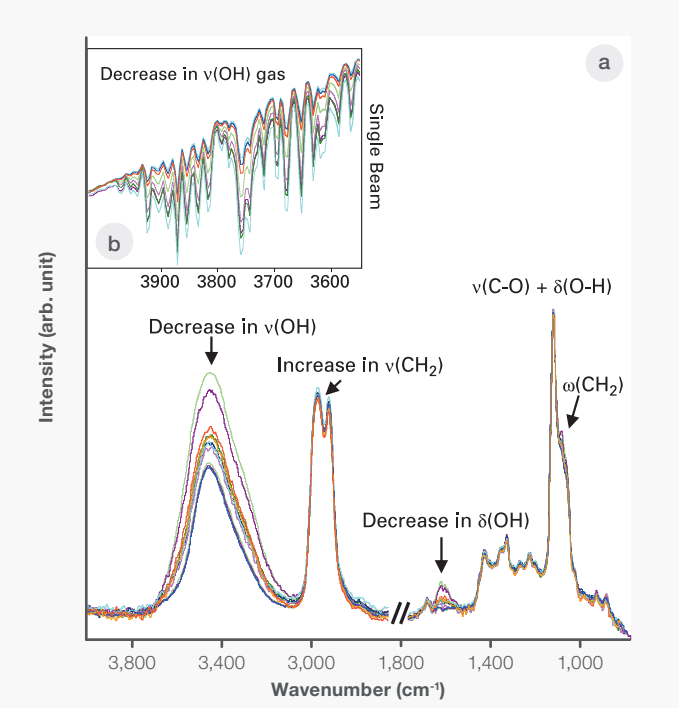

Figure 3. Changes in (a) EG2 spectra and (b) water vapor.

Summary

Moisture readily adsorbs on a hydrophilic EG2-modified amorphous carbon surface. PM-IRRAS dual modulation isolates surface signal from isotropic gas phase signal, allowing real-time monitoring of water desorption without interferences from gas phase signal which normally obscures weak surface signal in single channel measurements.

Changes in the $\nu(CH_2)$ region suggests changes in the average carbon chain orientation of EG2 as water leaves the surface. This demonstrates the possibility of using these modified surfaces for biosensing applications.

Acknowledgement

GWC Technologies provided the sample and the SSD100 demodulator photograph.

Reference

1. B. Sun; P. E. Colavita; H. Kim; M. Lockett; M. S. Marcus; L. M. Smith; R. J. Hamers *Langmuir* 2006, 22, 9598.
2. M. R. Lockett; J. C. Carlisle; Dinh V. Le; L. M. Smith *Langmuir* 2009, 25, 5120.

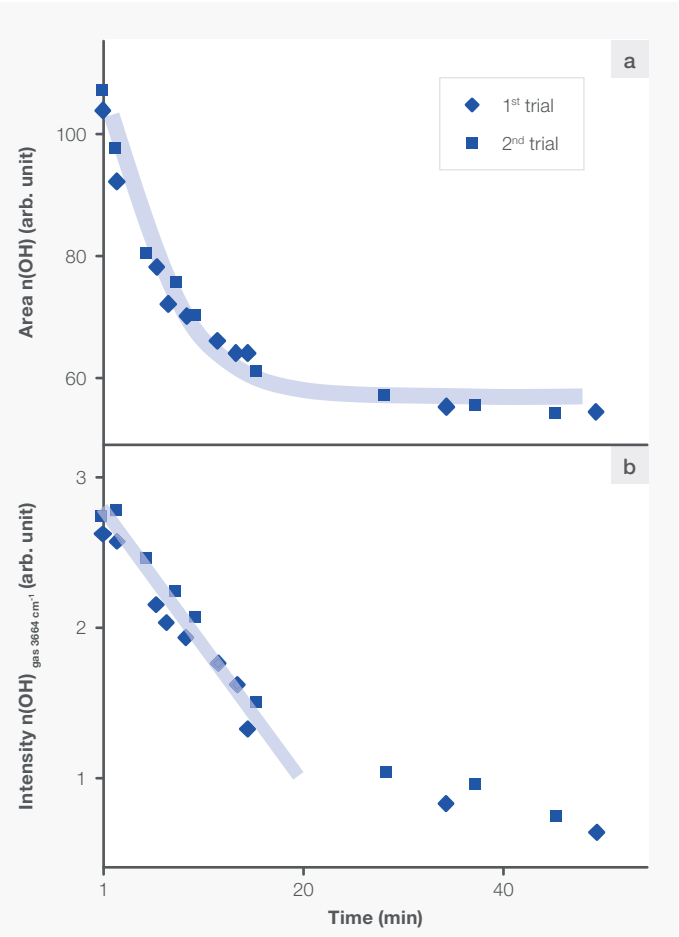

Figure 4. Changes in (a) integrated area of liquid water ν(OH) and (b) intensity of gas phase water ν(OH) band with time.