

Direct Analysis of Oxidizing Agents in Aqueous Solution with Attenuated Total Reflectance Mid-Infrared Spectroscopy and DLC Protected Waveguides

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Abstract

A novel approach for the direct detection of oxidizing agents in aqueous solution is presented using diamond like carbon (DLC) protected waveguides in combination with attenuated total reflectance (ATR) mid-infrared spectroscopy. Pulsed laser deposition (PLD) was applied to produce high quality DLC thin films on ZnSe ATR crystals with thicknesses of a few 100 nm. Scanning electron

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microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) has been used to investigate the surface properties of the DLC films including the $sp^3:sp^2$ hybridization ratio of the carbon bonds. Beside excellent adhesion of the DLC coatings to ZnSe crystals these films show high chemical stability against strongly oxidizing agents. IR microscopy was utilized to compare differences in the chemical surface modification of bare and protected ATR waveguides when exposed to hydrogen peroxide, peracetic acid and ammonium persulfate. The feasibility of DLC protected waveguides for real-time concentration monitoring of these oxidizing agents was demonstrated by measuring calibration sets in a concentration range of 0.2 % to 10 %. Additionally, principal component regression (PCR) has been applied to analyze multicomponent mixtures of hydrogen peroxide, acetic acid and peracetic acid in aqueous solution. Due to high chemical stability and accurate monitoring capabilities DLC protected waveguides represent novel approach for directly detecting oxidizing agents in aqueous solution with promising potential for industrial process analysis.

Keywords: attenuated total reflection, ATR, infrared spectroscopy, FT-IR, pulsed laser deposition, diamond like carbon, DLC, thin film technology

1. Introduction

Over the past decades interest for on-line monitoring of strongly oxidizing agents has grown significantly due to numerous applications in wastewater and textile treatment, sterilization (CIP, clean-in-place), and chemical industry. In particular, peroxides such as hydrogen peroxide (HP) and peracetic acid (PAA) are increasingly used as they represent a viable alternative with higher oxidation potential to many of the routinely applied halogenated compounds. Additionally, improvements for safer and more efficient storage of peroxides (e.g. stabilization with phosphates and tin(IV) materials via hydro-colloid formation) have promoted their industrial application¹. Common to many of these applications are relatively high concentration levels. Resulting, in-situ analytical techniques, monitoring oxidant concentration levels online, demand robust sensor systems operable at harsh measurement conditions.

Reliable determination of HP and PAA is routinely performed by titration techniques utilizing compound specific differences of redox properties^{2,3}. Aside from such discontinuous methods hydrogen peroxide detection is performed by spectroscopic determination utilizing changes in color^{4,5}, fluorescence⁶⁻⁸ or chemiluminescence⁹⁻¹¹. All optical measurement techniques are based on the determination of reaction products following a chemical reaction between hydrogen peroxide and various reagents. Electrochemical methods for the determination of hydrogen peroxide can be divided into amperometric¹²⁻¹⁴, potentiometric¹⁵ and conductometric methods¹⁶, respectively. In particular, amperometric sensors offer the possibility of direct on-line monitoring. Due to the required overpotential noble metal electrodes, such as gold or platinum and metallized carbons^{17,18}, have been applied reducing the overpotential. Nevertheless, a significant potential is still required and interferences caused by other electroactive compounds may occur. Approaches to eliminate these obstacles by introducing the redox active enzyme horseradish peroxidase as biological catalyst have been reported in literature¹⁹. However, while this strategy enables very low operating potentials, issues

such as electrode fouling and enzyme stability are not yet solved when applying the sensor system for long-term concentration monitoring.

Peracetic acid is technically prepared from acetic acid and hydrogen peroxide in the presence of an acidic catalyst, typically H_2SO_4 ²⁰. Several analytical techniques for the determination of PAA including photometry²¹, spectrophotometry²², electrochemical sensing²³ and gas chromatography^{24,25} have been reported. In addition, simultaneous determination techniques for HP and PAA have successfully been demonstrated using HPLC²⁶, electroanalysis^{27,28} and via selective photometric determination of PAA in the presence of hydrogen peroxide²⁹.

Mid-infrared (MIR) spectroscopy is nowadays recognized as an analytical technique of persistently increasing importance. Continuous progress in development of MIR-transparent optical waveguides enables the extension of conventional IR spectroscopy towards spectroscopic sensing systems³⁰⁻³². Taking advantage of molecule specific vibrational and rotational transitions and their resulting distinctive absorption patterns in the MIR spectral range the development of compact sensor systems for selective multicomponent analysis is enabled^{33,34}. The majority of spectroscopic sensing systems increases selectivity and sensitivity by appropriate molecular recognition layers coated onto the waveguide surface serving as solid phase extraction membrane for the analytes of interest, while simultaneously excluding water from interaction with the evanescent field³⁵⁻³⁸. Sensors based on direct interaction of analytes with evanescently guided radiation and without chemical modification of the waveguide surface are more prone to interferences by IR absorbing compounds. Hence, they are limited to application for dedicated analytical problems in well-defined matrices and to considerably high analyte concentration levels in the mg/L range^{39,40}. In addition, many commonly applied waveguide materials with sufficient transparency in the spectral region of approx. 3-15 μm , such as zinc selenide (ZnSe), are susceptible to strong acids, bases and strongly oxidizing agents in general.

Consequently, protected waveguides using chemically inert thin film layers with minor spectral interference coated onto highly MIR transparent waveguides would be of great interest.

Recently, research in amorphous hydrogenated carbon films has been significantly promoted due to numerous unique properties including high level of hardness (up to 80 GPa), high resistivity (up to $10^{16} \Omega \text{ cm}^{-1}$), transparency over a wide optical range (optical band 1.0 – 4.0 eV) and chemical stability⁴¹. Diamond like carbon (DLC) is an important form of amorphous carbon composed of a mixture of sp^3 and sp^2 coordinated carbon. The beneficial properties of DLC derive from the sp^3 constituents making DLC mechanically robust, transparent in the infrared spectral range and chemically inert⁴². Besides the well-established methods of ion-plasma deposition, pulsed laser deposition (PLD) is particularly suitable for producing high quality DLC films^{43,44}. Due to their numerous advantages DLC coatings have found applications as hard protective coatings for magnetic disc drives, antireflective coatings for IR windows and field emission source for emitters⁴⁵⁻⁴⁷.

The focus of this study is to develop an on-line IR spectroscopic sensor system based on DLC protected IR waveguides for real-time concentration monitoring of strongly oxidizing agents used in disinfection, bleaching processes and waste-water treatment.

The feasibility of this system has been tested for hydrogen peroxide, peracetic acid and ammonium persulfate as target analytes. Thorough studies of the DLC thin film structure and properties including $\text{sp}^3:\text{sp}^2$ hybridization ratio of the carbon bonds are presented. Chemical and mechanical stability of the protective DLC layer against oxidizing agents and remaining transparency of DLC coated zinc selenide attenuated total reflectance (ATR) waveguides were analyzed. Calibration experiments demonstrate the suitability of the ATR measurement set-up to serve as on-line sensor system. Finally, principal component regression (PCR)⁴⁸⁻⁵⁰ has been used for calibration of the spectroscopic sensing system and successfully applied to multicomponent analysis of mixtures of hydrogen peroxide, acetic acid and peracetic acid in aqueous solution.

2. Experimental

Chemicals

Hydrogen peroxide (30 wt. % solution in water), ammonium persulfate, acetic acid and peracetic acid (32 wt. % solution in dilute acetic acid) were purchased from Aldrich (Milwaukee, WI, USA). Deionized water for dilution of the stock solutions was used throughout the experiments.

Preparation diamond like carbon films

The DLC coatings were fabricated by pulsed laser deposition using a home-made laboratory PLD coating system. An Electro-graphite target (99.5 % carbon, impurities of vanadium, titanium, hydrogen and oxygen) was used for the ablation of carbon applying a pulsed Nd:YAG laser, which provides a beam with a wavelength of 1064 nm, a pulse energy of 1 J, and a pulse duration of 10 ns at a repetition rate of 10 Hz⁵¹. The target was rotated during laser irradiation avoiding the formation of deep craters at the surface of the ATR crystal and to prevent ablation of droplets. The emitted species were deposited at room temperature (approx. 25 °C) in argon atmosphere onto ZnSe ATR elements (50*20*2mm, 45°, Macrooptica Ltd., Moscow, Russia). Prior to film deposition the substrates were cleaned in pure ethanol and dried with pure nitrogen. The film thickness was adjusted by varying the deposition time.

Film Characterization

The surface quality and growth structures of the DLC coatings were inspected with light microscopy and scanning electron microscopy (Cambridge Instruments Stereoscan 360).

X-ray photoelectron spectroscopy (XPS) was used to investigate the nature of chemical bonding in the coatings using an Omicron Multiprobe system with a monochromized AlK α (1486.6 eV) X-ray beam and an EA 125 energy analyzer. The spectrometer was operated in fixed analyzer energy transmission mode (FAT) at a base pressure of 4×10^{-9} Pa. The resolution of the selected set-up is better than 0.6 eV,

the detection sensitivity is approx. 1 vol.%. A sputter gun using Ar⁺ ions was applied for cleaning the samples prior to investigation.

Attenuated Total Reflectance (ATR) spectroscopy

IR radiation coupled into the ATR waveguide incident at the crystal/water interface at angles larger than the critical angle creates an evanescent field guided along that interface. Analyte molecules in vicinity to the waveguide absorb energy from the evanescently guided radiation at wavelengths in resonance with molecule-specific vibrational transitions. Signal detection and processing are achieved by Fourier transform infrared (FT-IR) analysis^{52,53}.

All measurements were performed with a Bruker IFS66 Fourier transform infrared (FT-IR) spectrometer (Bruker Optics, Billerica, MA, USA) equipped with a LN₂ cooled mercury-cadmium-telluride (MCT) detector (Infrared Associates, Stuart, FL, USA). A total of 100 scans was averaged for each spectrum at a spectral resolution of 4 cm⁻¹. For attenuated total reflectance measurements a vertical ATR accessory (Specac Inc. Smyrna, GA, USA) in combination with trapezoidal, DLC coated ZnSe ATR elements was used. In order to prevent chemical attack of the ATR flow cell assembly by the oxidizing agents a flow-cell made from plexiglass with dimensions 40x15x5 mm was developed. A VitonTM O-ring placed between the plexiglass channel and the ATR crystal seals off the cell creating a sample volume of 0.5 mL. A peristaltic pump (C8-Midi, Watson-Marlowe Alitea, Sweden) assured a constant flow rate of aqueous analyte solution through the flow cell at 3 mL/min.

Prior to sample measurements deionized water was pumped through the cell until no significant changes of the water absorption bands occurred and a background spectrum was recorded. Sample solutions with increasing analyte concentration were measured by collecting spectra in intervals of 1 min for a period of 5 min.

3. Results and discussion

Preliminary experiments have shown that strongly oxidizing agents such as peracetic acid immediately chemically degrade ZnSe crystals due to formation of H_2Se^{54} . H_2Se is subsequently oxidized by hydrogen peroxide or peracetic acid to reddish Se, which has been observed at the surface of unprotected PAA treated ZnSe ATR crystals. As this degradation significantly reduces the optical throughput of the waveguide appropriate protective surface layers are a basic necessity. DLC films deposited onto ZnSe waveguides with a thickness of max. 200 nm provide the required chemical and mechanical stability against oxidizing agents, while maintaining the optical transmission properties of the waveguide in the required spectral window.

Structure and properties of the DLC coatings

Figure 1 shows a typical SEM micrograph of a cross fracture section of a DLC coating with a thickness of approx. 1 μm deposited onto a steel substrate. Besides the dense coating structure a very smooth surface with only a few defects (e. g. larger particulates ablated from the target) can be observed. X-ray diffraction (XRD) investigations indicate an amorphous film structure. XPS investigations of the C(1s) peak lead to a sp^3 carbon bond content of about 36 %. These values were evaluated by fitting the C(1s) peak with the two main components diamond represented by sp^3 bonding (peak at 285.2 eV) and graphite represented by sp^2 bonding (peak at 284.4 eV) and by calculating the area fractions beneath the peaks⁵⁵. Furthermore, small contents of C-O bonds were detected. The contribution of the background was approximated by the Shirley method. The XPS spectra of the film and the deconvolution into contents corresponding to diamond and graphite, respectively, are shown in Figure 2. The relatively low sp^3 content of the coating is in agreement with Voevodin's observation of the growth of mainly graphitic films produced by PLD of carbon when employing 1064 nm Nd:YAG laser radiation at laser pulse power densities lower than $10^{11} \text{ W cm}^{-2}$.

Investigation and application of DLC coated ZnSe waveguides

Crucial parameters for any type of protective layer deposited at the surface of MIR waveguides include that: (i) the material should have a suitable spectral window in the wavelength region of interest, (ii) a minimum of spectrally interfering IR absorptions reducing optical radiation losses within the waveguide and (iii) chemically protective properties at film thicknesses < 200 nm, which still enables sufficient penetration of the evanescent field into the adjacent medium. Usually, hydrophobic organic polymers with a layer thickness in the range of 1-10 μm are applied as coating materials, as they exclude water being a strong IR absorber from the analytical volume probed by the evanescent field. Furthermore, enrichment capabilities for non-polar organic analytes are advantageous if low detection limits are required. Alternatively, sol-gel membranes have recently been investigated providing significant suppression of the water background while enriching environmentally relevant compounds⁵⁶⁻⁵⁹. Due to the fact that the diffusion process of analytes into the enrichment membrane limits the sensor response time. This study was focused on highly inert, thin layers of diamond like carbon deposited onto the surface of ZnSe crystals for direct determination of oxidizing agents in aqueous solution at concentrations $> 0.1\%$ (vol). These films should demonstrate sufficient mechanical and chemical stability combined with rapid sensor response. In Figure 3 single beam spectra of a bare (c) ZnSe waveguide and crystals coated with either 100 nm (b) or 200 nm (a) DLC layers are shown. As expected, deposition of a thicker DLC film results in reduced transmission though even a 200 nm film still provides sufficient energy throughput for quantitative detection in the percentage concentration range. In particular, the provided spectral window in the wavelength region from 3000 cm^{-1} to 600 cm^{-1} with the low frequency cut-off determined by the MCT detector is of interest for practical applications as MIR detection of various classes of strongly oxidizing analytes is enabled. However, increasing absorption of the DLC layer above 2700 cm^{-1} limits the quantification of lower concentrated compounds.

Absorption features evident around 2900 cm^{-1} (C-H stretching vibrations) and in the fingerprint region of the single beam spectra are attributed to the absorbance of the sealing polymers which are in contact with the waveguide surface, i.e. a Teflon ring avoiding mechanical damage of the crystal by the plexiglass cell and a Viton ring creating the sample compartment for flow-cell experiments. Since a new background spectrum is recorded before each sample measurement, these absorption features are eliminated in the resulting ATR spectrum.

Prior to ATR measurements the mechanical and chemical stability of the DLC layers was evaluated. Without application of solvents both layers (100 and 200 nm) revealed sufficient adhesion during application of frictional forces, e.g. rubbing resulted in no visible damage of the layer. When using acetone or ethanol in combination with frictional forces sections of the layer could be partially removed. Small drops of peracetic acid were applied to the interface and within few minutes formation of reddish Se as oxidation product was observed at the uncoated sections, while parts of the crystal which were still coated with the protective layer remained resistant. Consequently, effects of oxidizing agents were studied more extensively on ZnSe crystal surfaces with unprotected and coated sections covered with a 100 nm DLC layer, respectively. Interface regions were exposed to various strongly oxidizing agents, including hydrogen peroxide, peracetic acid and ammonium persulfate. Optical microscopy images and IR-microscopic data (a-d) were recorded at the treated surface sections of the crystals and are summarized in Figure 4. Compared to the DLC coated crystal the unprotected waveguide exhibits severe surface modifications independent from the type of oxidant, which is particularly evident in the interface region between the undamaged surface (lower left corner of images in Figure 4) and the chemically attacked section. Microscopic images of freshly prepared DLC coated waveguides were compared to images of DLC coated waveguides after the chemical stability studies resulting in no visible alteration of the surface. To further corroborate the indicated inertness of DLC protected crystals localized spectra measured by IR microscopy of areas exposed to oxidizing agents

during the chemical stability experiments were analyzed. Either an unmodified ZnSe crystal surface or a freshly prepared DLC coated surface has been used as background spectrum. Except for the characteristic CO₂ stretching vibration around 2350 cm⁻¹ the absorbance spectrum of the DLC coated crystal surface remains constant before and after oxidant treatment, which indicates that no chemical modification has occurred (d). In contrast, each oxidizing agent can be identified by several characteristic absorption bands after treatment of the uncoated crystal sections. In case of hydrogen peroxide (b) and peracetic acid (c) O-H stretching and deformation vibrations are evident, which gives reason to believe that during the oxidation process Zn(OH)₂ is formed at the surface. Treatment with ammonium persulfate provides less pronounced O-H vibrations with residual NH₄⁺ present characterized by absorptions around 1400 cm⁻¹. This reaction seems to be supported by the appearance of a strong SO₄²⁻ vibrational mode at 1100 cm⁻¹, which indicates ZnSO₄ formation.

As the application of DLC protected waveguides for strongly oxidizing agents is envisaged, IR spectra of the investigated analytes hydrogen peroxide (b), peracetic acid (c) and ammonium persulfate (d) are presented in Figure 5. In addition, the spectrum of acetic acid (a) is shown since aqueous peracetic acid solutions usually consist of 32 % peracetic acid, 40-45 % acetic acid and approx. 6 % H₂O₂. The main IR absorption features are labeled and summarized in Table 1. Since peracetic acid is only stable in equilibrium with acetic acid and hydrogen peroxide, the respective absorbance spectrum is actually a superposition of three spectra. In addition to compound specific spectral features including the O-H deformation vibration (H2) and all major vibrational modes of acetic acid (A1, A2, A3) the spectrum of peracetic acid shows two main peaks at 1758 cm⁻¹ (P1) and 1217 cm⁻¹ (P3). These shifted bands are caused by the electronegative peroxide group facilitating differentiation between the two organic acids. The corded areas in the spectra indicate the absorption bands used for quantification of the ATR measurements by calculating either the peak height or peak area during non-chemometric data evaluation of individual compounds. Figure 6 demonstrates the correlation between the concentration

of oxidizing agents and peak height or peak area, respectively, evaluating δ (O-H) for H_2O_2 at 1382 cm^{-1} , δ (C-O-O-H) for peracetic acid at 1217 cm^{-1} and ν_{as} (SO_4^{2-}) for ammonium persulfate at 1272 cm^{-1} . Seven analyte concentrations in a range from 0.2 % up to 10 % were consecutively detected three times additionally providing the mean and standard deviation of the repeated measurements (Figure 6). The quality of the linear fit is given by the correlation coefficient and shows excellent linear behavior for all investigated oxidants with relative standard deviations generally $< 2.5\%$ for each individual concentration value. Only data recorded for 0.2 % concentrations results in relative standard deviations up to 10 % as these values are close to the limit of detection (LOD) of the applied direct measurement technique. From the initial slope of the calibration functions and the standard deviation of blank measurements (deionized water) the following LODs were determined for each analyte with DLC surface protected (100 nm) ZnSe ATR crystals: (i) 0.07 % for H_2O_2 , (ii) 0.05 % for peracetic acid and (iii) 0.01 % for ammonium persulfate. These LODs are sufficient for most practically relevant applications of the investigated oxidants as usually concentrations $> 0.1\%$ are encountered in wastewater treatment, chemical processes, sterilization baths and bleaching processes.

As aforementioned, peracetic acid is only stable in presence of H_2O_2 and acetic acid. Hence, for thorough analysis of peracetic acid samples using the developed IR-ATR technique with DLC surface protected waveguides strongly overlapping spectral features of these compounds have to be taken into account (Figure 5). Hence, chemometric data evaluation techniques were applied for improved data handling. Principal component regression (PCR)⁴⁸⁻⁵⁰ was selected as viable approach for multivariate concentration evaluation of aqueous mixtures simultaneously containing peracetic acid, H_2O_2 , and acetic acid. Since PCR is based on multivariate least squares regression^{60,61}, all information contained in a measurement spectrum, i.e. many independently measured absorbances, are used to determine concentration values of the calibrated analytes providing precise results. The main advantage of PCR over classical multivariate regression algorithms, which directly evaluate Beer's law, is that not all

absorbers contained in the calibration set must be known. Only the substances of interest have to be calibrated; PCR implicitly includes effects of unknown matrices, i.e. other chemicals at changing concentration into the calibration model under the premise that these effects have already been present in the calibration data. For instance, it was observed that measurement signals nonlinearly increasing with concentration changes can be correctly evaluated by PCR methods⁶².

The calibration set in this example consisted of five acetic acid samples (1 %, 2.5 %, 5 %, 7.5 %, and 10 % dissolved in water), seven H₂O₂ samples (0.2 %, 0.6 %, 1 %, 2.5 %, 5 %, 7.5 %, and 10 % dissolved in water) and two peracetic acid samples (0.64 % and 2.67 % dissolved in water). The latter samples also contained 0.8 % and 3.34 % acetic acid, as well as 0.12 % and 0.5 % H₂O₂. From the spectra of these samples the PCR calibration step extracted three relevant principal components defining the calibration model for this application. Derived from the PCR calibration, five peracetic acid samples (0.21 %, 0.43 %, 0.85 %, 1.08 %, 5.36 %) were evaluated to simultaneously determine their peracetic acid, acetic acid and H₂O₂ content and to validate the calibration model. In Figure 7 the PCR results of all three compounds are plotted vs. the input concentrations. The input concentrations and the calibration concentrations were determined assuming following concentrations in the stock solution: 32.2 % peracetic acid, 4.83 % H₂O₂ (determined by the titration method of Greenspan⁶³) and 40 % acetic acid (according to the bottle label of Sigma Aldrich). As can be seen from Figure 7, with exception of the sample with the highest concentration the measured concentrations are in very good agreement with the input values. The variation in the data for the highest concentration is due to shifts in the corresponding spectra, which are more pronounced for this concentration when compared to other data sets. Apart from the highest concentration value the errors are at the order of 0.02 % for peracetic acid and H₂O₂, and 0.08 % for acetic acid.

Outlook

Nowadays, chemometric methods for calibration of spectrometers and evaluation of spectra are standard methods. For on-line process applications the determination of analyte concentrations has to be automated and independent from user interaction. These demands are fulfilled by chemometric algorithms like principal component regression (PCR). However, the standard approach is usually not robust enough with respect to long-term drifts and incomplete calibration information. Occurrence of drifts or uncalibrated spectral features is commonly encountered in unsupervised process measurements. Since drifts usually result in wrong concentration results, frequent and expensive recalibration of the device is necessary. Uncalibrated spectral features must be detected and corrected to avoid deriving wrong concentration values. Furthermore, during on-line process monitoring applications recognition of disturbances is particularly relevant since they may indicate quality problems or even process failures. Recognition of such disturbances is especially valuable for tracking the origin of the disturbance. Hence, chemometric data evaluation has to be inherently prepared for handling uncalibrated spectral features. Drift correction and detecting uncalibrated absorption features must be done for every single measurement spectrum individually and without any a priori information. To accomplish this, conventional PCR was recently augmented by a drift correction algorithm^{64,65} and a preprocessing step to correct for uncalibrated absorption features^{66,67}. Combined application of both algorithms has recently been achieved and will be reported in the near future⁶⁸.

4. Conclusions

We present a novel approach using diamond-like-carbon (DLC) films as protective coatings on ZnSe ATR crystals for direct analysis of strongly oxidizing agents in aqueous solution. Pulsed laser deposition (PLD) allows the formation of thin DLC films (< 100 nm) yielding a new generation of mid-IR waveguides with excellent mechanical and chemical stability. Detection of various oxidizing agents such as hydrogen peroxide, peracetic acid and ammonium persulfate, and application of

chemometric algorithms for multicomponent evaluation demonstrates the potential of surface modified mid-IR optical sensors for on-line monitoring at harsh industrial conditions.

Hence, new opportunities for accurate analysis of wastewater, sterilization bath or leaching processes can be envisaged, e.g. the determination of hydrogen peroxide in cellulose fiber or paper bleaching baths⁶⁹. In addition, chemometric algorithms are applied providing precise multivariate data evaluation in such complex matrices. Since on-line measurement techniques are a challenging task for spectroscopic data evaluation, extended algorithms are currently in development, which allow for dynamical adjustment of background drifts and correction of interfering uncalibrated spectral features. These augmented algorithms are expected to play a major role in future applications of chemometrics in process control.

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Tables

Table 1

	Label	Peak position (cm^{-1})	Type of vibration
Acetic acid	A1	1710	$\nu(\text{C}=\text{O})$
	A2	1390	$\nu(\text{C}-\text{O})$
	A3	1276	$\delta(\text{C}-\text{O}-\text{H})$
Hydrogen peroxide	H1	2832	$\nu(\text{O}-\text{H})$
	H2	1382	$\delta(\text{O}-\text{H})$
Peracetic acid	P1	1758, 1712	$\nu(\text{C}=\text{O})$
	P2	1390	$\nu(\text{C}-\text{O})$
	P3	1276, 1217	$\delta(\text{C}-\text{O}-\text{O})$
Ammonium persulfate	S1	1452	$\nu(\text{NH}_4^+)$
	S2	1272	$\nu_{\text{as}}(\text{SO}_4^{2-})$
	S3	1048	$\nu_{\text{s}}(\text{SO}_4^{2-})$

Figures

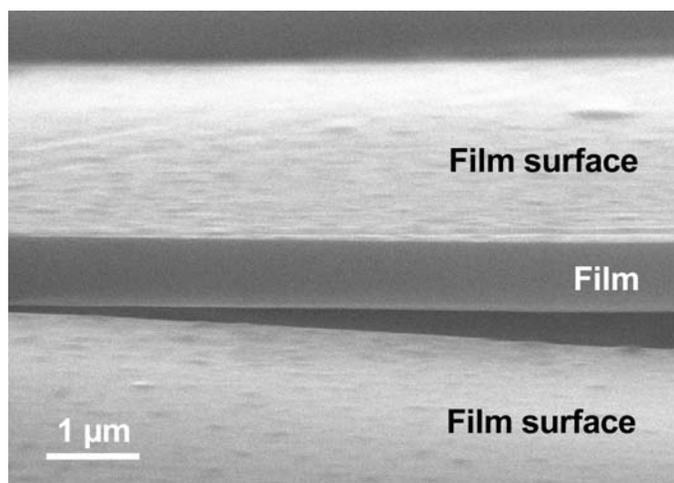


Figure 1:

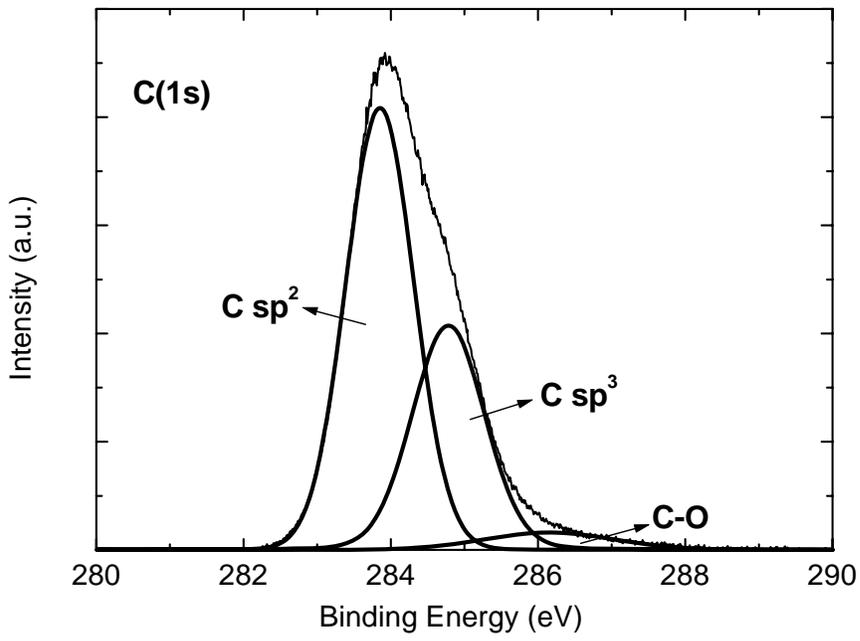


Figure 2:

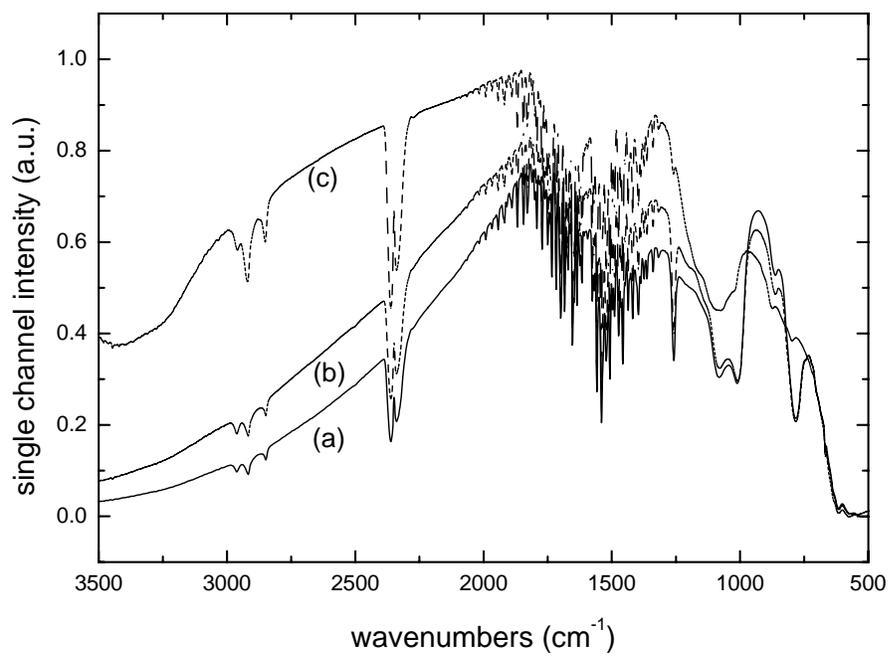


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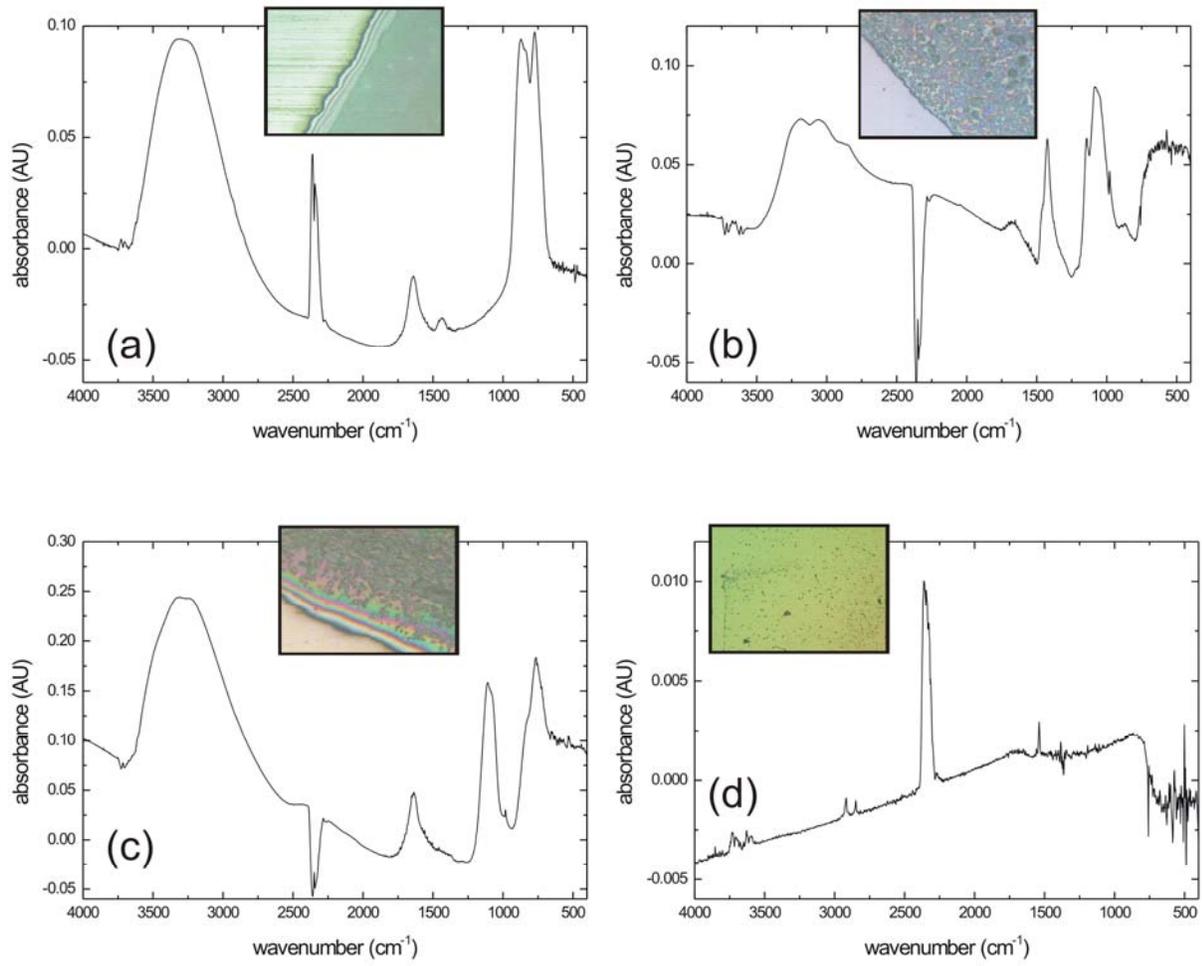


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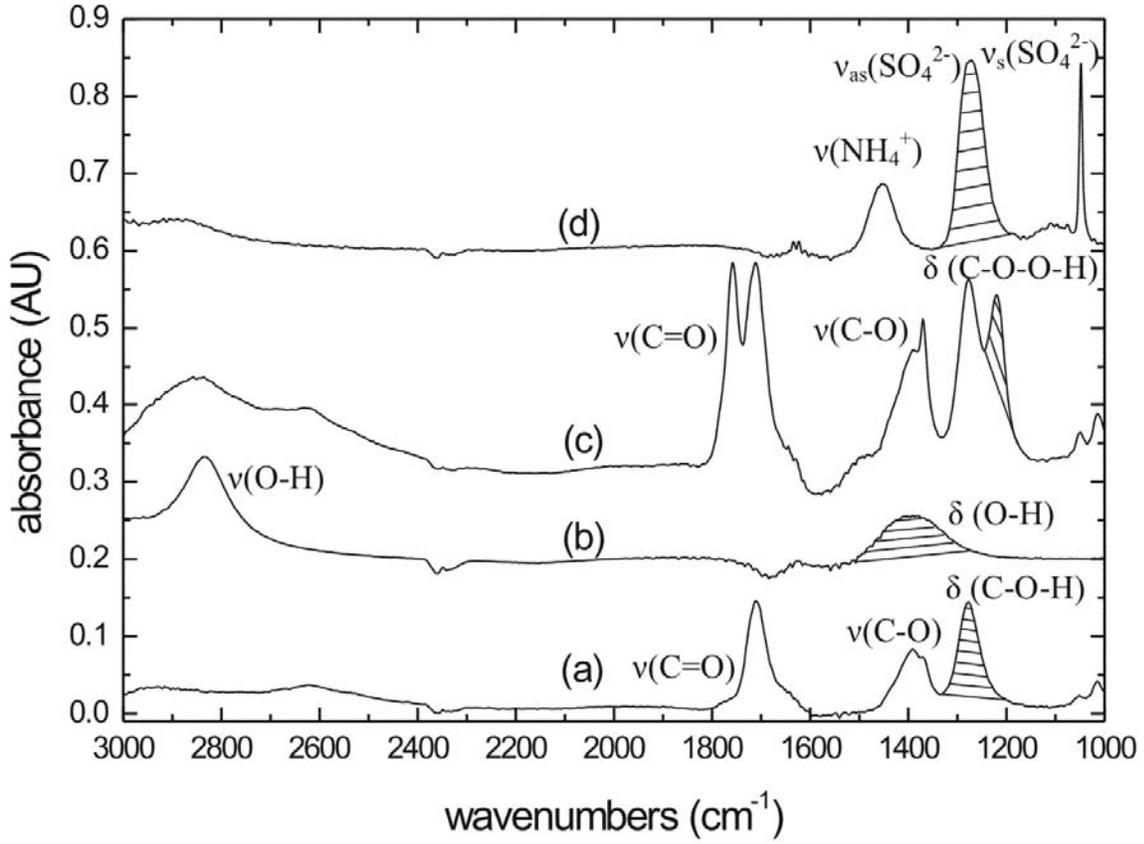


Figure 5:

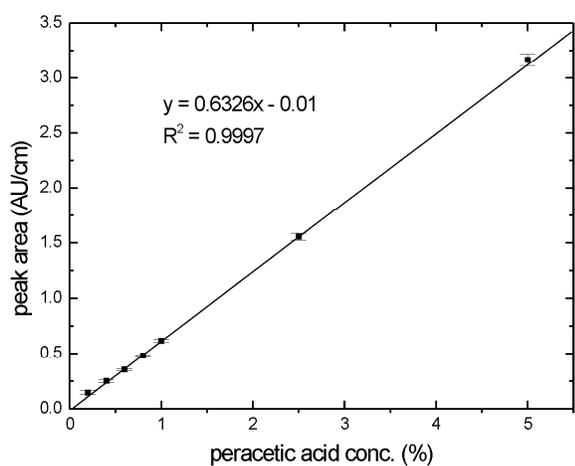
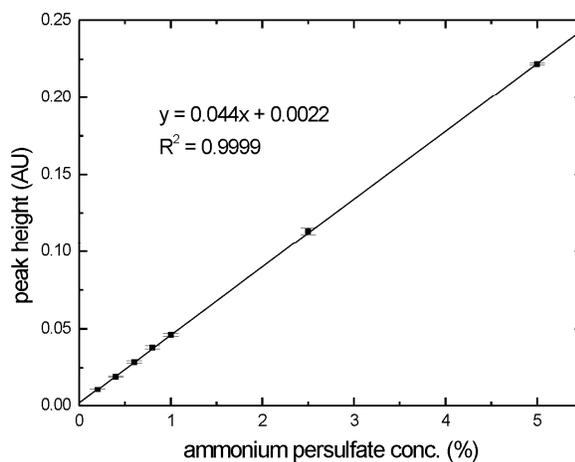
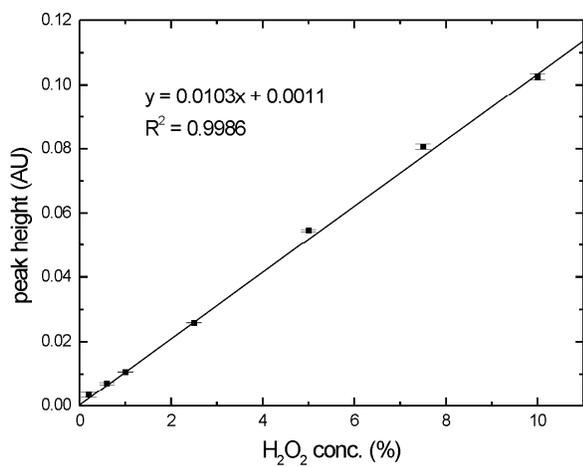


Figure 6:

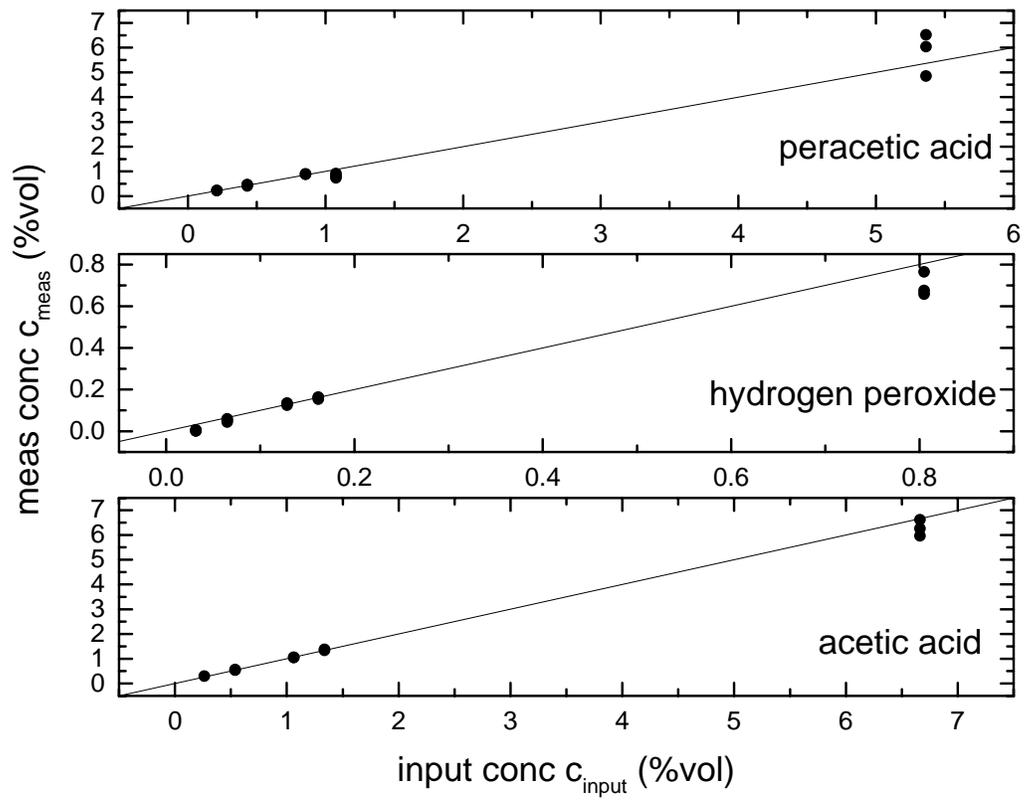


Figure 7:

Table and Figure Captions

Table 1: Analyte specific vibrational IR features of (a) acetic acid, (b) hydrogen peroxide, (c) peroxyacetic acid and (d) ammonium persulfate.

Figure 1: SEM micrograph of a fracture section of DLC film indicating a dense film structure and a smooth film surface.

Figure 2: XPS spectra of the C(1s) peak of a DLC film and the deconvolution of the measured cumulative peak, the sp^2 , sp^3 and C-O peaks, each being a mixture of a Gaussian and Lorentzian peak.

Figure 3: Single beam spectra of (a) bare ZnSe crystal and ZnSe crystals coated with (b) 100 nm DLC thick films and (c) 200nm DLC thick films.

Figure 4: Optical and IR microscopic images of (a) bare ZnSe crystal treated with hydrogen peroxide, (b) bare ZnSe crystal treated with ammonium persulfate (c) bare ZnSe crystal treated with peroxyacetic acid and (d) 100 nm thick DLC coated ZnSe crystal treated with peroxyacetic acid (Resolution opt. images: 100x magnification; parameters for IR-Mic. images: transmission mode, spectral res.: 4 cm^{-1} , spot size: 1x1 mm).

Figure 5: IR absorbance spectra of aqueous analyte solution (5 % v/v) of acetic acid (a) hydrogen peroxide (b), peroxyacetic acid (c) and ammonium persulfate (d).

Figure 6: Calibration curves of hydrogen peroxide, ammonium persulfate and peroxyacetic acid.

Figure 7: Results of the principal component regression evaluation of peroxyacetic acid, H_2O_2 , and acetic acid; the straight function indicate where $c_{\text{meas}} = c_{\text{inp}}$.

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