Determination of Q_{st} for CO_2 adsorption in a microporous polymer

Insplorion's Nanoplasmonic Sensing (NPS) technology enables sensitive detection of changes in the effective refractive index within a sensing volume that extends a few tens of nanometers from the NPS sensor surface. In this application note the NPS technology is used to monitor the adsorption of CO_2 molecules within a microporous polymer adsorbent (PIM-1). By studying the NPS signal dependence on the partial pressure of CO_2 gas and temperature, adsorption isotherms can be constructed and the *isosteric heat of adsorption* (Q_{st}) calculated.

Introduction

Carbon capture and storage (CCS) in micro- and mesoporous materials is an interesting route to CO_2 emission reduction. In order for CCS to be more viable at a large scale, it is desired to develop novel more cost-efficient materials that are CO_2 selective. Materials successful at capturing CO_2 are engineered such that the strength of the adsorbent-CO_2 molecule interaction is optimal. This interaction is characterized by the *isosteric heat of adsorption* (Q_{st}).

In this application note, Insplorions nanoplasmonic sensing (NPS) technology is used to study the interaction between CO_2 and a microporous polymer (PIM-1).

NPS allows studying the interaction in real-time under relevant conditions (different partial pressures and temperatures) and the results can be used to calculate Q_{st}.

Experimental Procedure

NPS substrates with a 10 nm thin coating of Si_3N_4 were spin-coated with PIM-1 solution (20 mg/mL in THF).

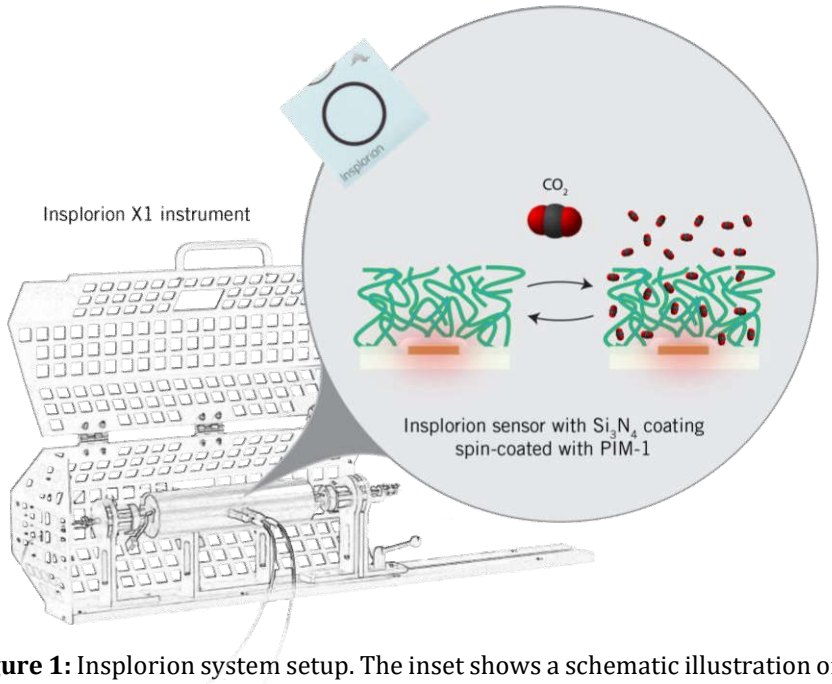

Figure 1: Insplorion system setup. The inset shows a schematic illustration of the sensor and sample configuration used in this application example (not to scale).

The resulting PIM-1 film thickness was 610 nm.

The samples were mounted in the quartz tube gas flow reactor system of the Insplorion X1 instrument. The sample was then heated and dwelled at the set temperature for one hour under constant flow of Ar (100 mL/min). The CO_2 loading/unloading cycles were then studied by sequentially flowing 1-1-0.25-0.5-0.75-1 atm of CO_2 gas. Each CO_2 loading step was performed for 15 min followed by an intermittent 15 min unloading step (100% Ar). The two initial 1 atm cycles where performed to activate the sample for CO_2 sorption. The same gas cycling sequence was performed at seven different set temperatures in the range 298-358°K). During the measurements the shift in position of the LSPR peak ($\Delta\lambda_{peak}$) was monitored as a function of time. The change in extinction at 450 nm (attributed to the absorption of PIM-1) was also recorded.

Insplorion AB • Medicinaregatan 8A • 413 46 Gothenburg • Sweden
Tel: +46 (0)31 380 26 95
Web: www.insplorion.com
E-mail: info@insplorion.com

Results

As can be seen in Figure 2B, the $\Delta\lambda_{peak}$ signal is correlated to the different exposure conditions (partial pressure and temperature) of CO_2. The sensing volume of NPS extends a few tens of nanometers into the PIM-1 film, therefore the signal is expected to be proportional to the amount of CO_2 adsorbed close to the internal substrate-polymer interface. The PIM-1 absorption band also exhibited changes in extinction correlated to the CO_2 exposure conditions. (Data shown in the full paper, [1]). Contrary to the NPS response, the intrinsic optical response of the PIM-1 film is proportional to adsorption throughout the film. These two signal are linearly correlated indicating that they carry identical information, however, the S/N ratio for the NPS measurement (228) is at least three times higher than for the intrinsic PIM-1 response (71).

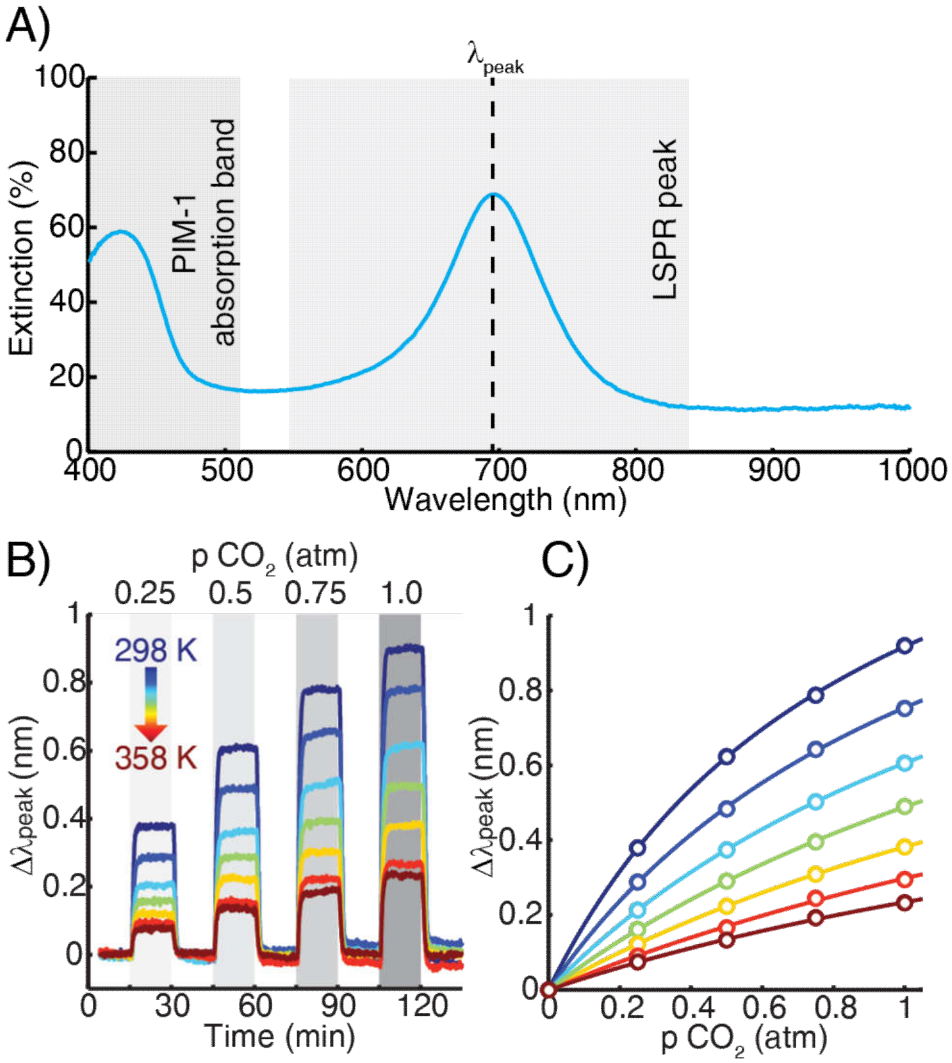

Figure 2: A) Extinction spectra for the NPS sensor with spin-coated PIM-1. The PIM-1 absorption band is well separated from the plasmon peak. B) Time resolved NPS response during sorption cycles of CO_2 at different partial pressures and temperatures. C) Optical CO_2 adsorption isotherms constructed from the data in B.

Langmuir adsorption isotherms are constructed by plotting the $\Delta\lambda_{peak}$ values vs. $p(CO_2)$ for the different temperatures (Figure 2C). Assuming that the NPS signal is proportional to the coverage, first order Langmuir adsorption gives:

$$\Delta\lambda_{peak} \propto q_{sat}\frac{Kp_{CO2}}{1+Kp_{CO2}}, \text{ (eq. 1)}$$

wherein q_{sat} is the saturation coverage and K is the adsorption equilibrium constant. The solid lines in Figure 2C represents fits to eq. 1. Q_{st} is found by plotting ln(K) vs. 1/T. The resulting value of ~29 kJ/mol is in excellent agreement with the value of 28.4 kJ/mol reported in literature.

Conclusions

NPS is an excellent method to directly measure the amount of adsorbed CO_2 with high S/N ratio. The method can be employed on any adsorbent, whether transparent or not, and enables quantitative analysis of adsorption equilibrium constants and energetics.

Note

[1] This study was performed at Chalmers University of Technology, Sweden. The full study is published in Analytical Chemistry: *"UV-Visible and Plasmonic Nanospectroscopy of the CO_2 Adsorption Energetics in A Microporous Polymer"*. Ferry A.A. Nugroho, Chao Xu, Niklas Hedin, and Christoph Langhammer.
Anal. Chem. 2015. DOI:10.1021/acs.analchem.5b03108

Insplorion AB • Medicinaregatan 8A • 413 46 Gothenburg • Sweden
Tel: +46 (0)31 380 26 95
Web: www.insplorion.com
E-mail: info@insplorion.com

Insplorion

Insplorion AB • Medicinaregatan 8A • 413 46 Gothenburg • Sweden
Tel: +46 (0)31 380 26 95
Web: www.insplorion.com
E-mail: info@insplorion.com