UV–Visible and Plasmonic Nanospectroscopy of the CO₂ Adsorption Energetics in a Microporous Polymer

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Supporting Information

ABSTRACT: In the context of carbon capture and storage (CCS), micro- and mesoporous polymers have received significant attention due to their ability to selectively adsorb and separate CO₂ from gas streams. The performance of such materials is critically dependent on the isosteric heat of adsorption \(Q_{st}\) of CO₂ directly related to the interaction strength between CO₂ and the adsorbent. Here, we show using the microporous polymer PIM-1 as a model system that its \(Q_{st}\) can be conveniently determined by \textit{in situ} UV–vis optical transmission spectroscopy directly applied on the adsorbent or, with higher resolution, by indirect nanoplasmonic sensing based on localized surface plasmon resonance in metal nanoparticles. Taken all together, this study provides a general blueprint for efficient optical screening of micro- and mesoporous polymeric materials for CCS in terms of their CO₂ adsorption energetics and kinetics.

Atmospheric CO₂ is in the spotlight in the wake of constantly increasing global temperature, where it is pinned as the single most important factor in the anthropogenic greenhouse effect. Therefore, numerous mitigation strategies for CO₂ emission reductions are suggested or already actively being applied. One particular direction is the CCS scheme, which has accelerated the search for materials that can capture CO₂ at a lower cost than today’s. In this context, micro- and mesoporous materials such as polymers, zeolites, or metal–organic frameworks (MOFs) have received particular attention. Capture of CO₂ with these materials exploits that CO₂ selectively adsorbs from gas mixtures and can be recovered as nearly pure CO₂ by cyclically increasing the temperature or decreasing the pressure. For a successful CO₂ capture, the CO₂–adsorbent interaction strength should be engineered in an optimal way. This interaction is typically assessed by measuring the isosteric heat of adsorption \(Q_{st}\) using gravimetric, volumetric, calorimetric, or to some extent chromatographic (carrier gas) techniques. The latter are simple and inexpensive but not very accurate. Calorimetric techniques are complicated by buoyancy and Knudsen diffusion at low pressure, volumetric techniques need accurate dead space determinations for volume correction, and calorimetric techniques are expensive and complex. Furthermore, porous polymer systems (as well as, e.g., MOFs) potentially show swelling upon CO₂ adsorption, which further complicates traditional analysis.

As an alternative approach, we show here that accurate direct measurements of the \(Q_{st}\) of CO₂ for microporous polymers become conveniently available by (i) \textit{in situ} UV–vis optical spectroscopy directly applied on the adsorbent or (ii) by indirect nanoplasmonic sensing (INPS) based on localized surface plasmon resonance (LSPR) in metal nanoparticles. As we show, INPS has a higher resolution than traditional spectroscopy owing to the superior sensitivity of plasmonic sensors. We use gold plasmonic sensor nanodisks with dimensions in the 100 nm size range on a transparent support. The nanodisks and the support (Figure 1) are coated with a 10 nm thick dielectric spacer layer to tailor the surface chemistry (here we used Si₃N₄). The INPS sensors monitor the surface specific changes occurring on the spacer layer or in its close vicinity via the strongly enhanced plasmonic electromagnetic field, which extends a few tens of nanometers beyond the spacer layer surface. Since the adsorbed CO₂ molecules slightly change the refractive index of the adsorbent within the enhanced field region, a spectral shift of the plasmon extinction peak (\(\lambda_{\text{peak}}\)) is induced, which is used as the readout with a reported resolution limit of 0.01 nm.

To demonstrate and benchmark our approach, we use a well-established polymer with intrinsic microporosity, PIM-1, as a CO₂ adsorbent model system. This class of polymers is attractive for CCS and other gas separation processes as they are easy to prepare and process, and have high gas permeability and selectivity. In addition, PIM-1 exhibits a light absorption band below \(\sim 480\) nm, which makes direct UV–vis spectroscopy with reasonable optical contrast possible. A schematic depiction of our approach and sample design is shown in Figure 1. The PIM-1 is deposited as a thin film on an INPS sensor chip by spin coating.
A typical extinction spectrum for the INPS chip with the thin PIM-1 film is also shown in Figure 1. It has two distinct bands: one in the near UV region from the PIM-1, and a second one, labeled by \( \lambda_{\text{peak}} \), at \( \sim 700 \) nm, from the LSPR of the Au nanodisks. To separate these two peaks, we tune the spectral position of the LSPR peak by tailoring the dimensions of the nanodisks. This spectral separation allows us to address both bands simultaneously but independently as plasmonic (by sensing of dielectric changes upon CO\(_2\) sorption via the LSPR) and intrinsic optical (by extinction at the PIM-1 absorption band), as responses to the CO\(_2\) pressure. The \( \Delta \lambda_{\text{peak}} \) corresponds to a local permittivity change due to \( \lambda_{\text{peak}} \) and the absorption band maximum of the PIM-1, as responses to the CO\(_2\) pressure. \( \Delta \lambda_{\text{peak}} \) exhibits the same changes and corroborates an intrinsic optical information obtained from both UV–vis readouts, respectively.

As shown in Figure 3a,b, the \( \Delta \lambda_{\text{peak}} \) readouts during the CO\(_2\) exposure of the PIM-1 film directly indicate variations in the amount of CO\(_2\) adsorbed in the polymer with respect to partial pressures (ranging from 25–100% of 1 atm in 25% steps) and temperatures (298–358 K in 10 K steps). Specifically, we notice the direct correlation between the CO\(_2\) concentration and temperature, and the magnitude of \( \Delta \lambda_{\text{peak}} \) which is in line with the expected pressure and temperature dependence of the amount of adsorbed CO\(_2\) in the polymer.

The correlation between the \( \Delta \lambda_{\text{peak}} \) signals is quantified by plotting the equilibrium \( \Delta \lambda_{\text{peak}} \) values for each pressure and temperature condition as a function of the corresponding \( \Delta \lambda_{\text{peak}} \), as displayed in Figure 3c. Their linear relation almost perfectly converges toward the origin and corroborates that identical information is obtained from both readouts. This scaling is quite remarkable as the two readouts are mechanistically very different. For example, the \( \Delta \lambda_{\text{peak}} \) is an integration throughout the whole PIM-1 film, i.e., the signal is the result of the sum of all CO\(_2\) molecules adsorbed in the sample. In contrast, plasmonic sensing only detects CO\(_2\) adsorbed within the PIM-1 in a vicinity of a few tens of nm.
Thus, our isotherms display perfect resemblance to the isosteres and Clausius–Clapeyron regression. The gray areas denote the regimes used for construction of isosteres and Clausius–Clapeyron regression analysis. The solid lines correspond to a linear regression between the ΔExtPM and Δλpeak derived from the equilibrium signals obtained at all investigated temperatures (color code) and CO₂ pressures (symbols). The dashed line denotes a linear regression with an R² value of 0.996.

Using the temperature and pressure dependent data obtained above, we can now construct CO₂ adsorption isotherms from the ΔExtPM and Δλpeak responses, as shown in Figure 4. The isotherms exhibit the expected dependencies on CO₂ partial pressure and temperature. Moreover, they are also in excellent agreement with first order Langmuir adsorption (solid lines, all regression parameters are available in the Supporting Information), as expected for CO₂ adsorption on glassy polymers.24 Thus, our isotherms display perfect resemblance with conventionally measured pressure–composition (p–C) isotherms reported for the same system.25,26 Therefore, the loading dependent Qst of CO₂ is extracted by means of a Clausius–Clapeyron analysis, as shown in the isosteres of Figure 5a, which are constructed from the p–T combinations in

Figure 3. Time resolved (a) ΔExtPM and b) Δλpeak signals upon CO₂ sorption cycles for different CO₂ partial pressures, carried out at different temperatures (298–358 K, 10 K steps). (c) Direct correlation between the ΔExtPM and Δλpeak derived from the equilibrium signals obtained at all investigated temperatures (color code) and CO₂ pressures (symbols). The dashed line denotes a linear regression with an R² value of 0.996.

Figure 4. Optical CO₂ adsorption isotherms constructed from (a) ΔExtPM and (b) Δλpeak at different temperatures (298–358 K, 10 K steps). The solid lines correspond to a first order Langmuir adsorption regression analysis. The gray areas denote the regimes used for construction of isosteres and Clausius–Clapeyron analysis of the loading dependent isosteric heat of adsorption.

Figure 5. (a) Isosteres for Clausius–Clapeyron analysis from ΔExtPM (red) and Δλpeak (blue) readouts at constant optical signal values, i.e., CO₂ coverage. (b) The isosteric heats of adsorption, Qst, obtained from the isosteres. Both analyses yield a very similar range of values between 27 and 31 kJ/mol. (c) Comparison of the loading dependent Qst values. Data obtained from the ΔExtPM the Δλpeak readouts of the INPS sensor sample, optical ΔExtPM measurement on a PIM-1 thin film directly on glass (i.e., without plasmonic nanoparticles) (green), and from conventional volumetric analysis of a PIM-1 sample synthesized in the same batch (purple). Note the good agreement between the different samples and detection modes as well as with the reported value from the literature, 28.4 kJ/mol (dashed line).26

Figure 4 at constant CO₂ coverage (corresponding to constant optical signal value).27 An alternative analysis based on the Langmuir model is shown in the Supporting Information.

The loading dependent Qst values are plotted in Figure 5b as a function of the optical signals ΔExtPM and Δλpeak which are proportional to the adsorptive loading of CO₂. Both optical readouts result in loading dependent Qst spanning a range of 27–31 kJ/mol. Moreover, as expected, we find that Qst is independent of the PIM-1 film thickness as shown in Figure S15 in the Supporting Information.

As the last step of our analysis, the Qst values are put in perspective. Figure 5c quantitatively compares the obtained numbers with additional results from an optical measurement with PIM-1 directly on glass (i.e., no plasmonic nanoparticles) as well as a sample characterized using conventional volumetric analysis (see the Supporting Information). Clearly, our optically derived results are in very good agreement with each other as well as with the 28.4 kJ/mol (dashed line) reported in the literature.26 The agreement with our Qst derived from the volumetrically determined isotherms (26–27 kJ/mol) is also very reasonable.

In summary, we demonstrate two simple yet very effective optical in situ characterization methods to reveal the adsorption energetics of CO₂ for porous materials targeting CCS or other...
CO$_2$/gas separation processes. They are based on UV−vis spectroscopy or nanoplasmonic sensing. Specifically, we observe CO$_2$ adsorption isothersms by either monitoring the direct optical extinction change of the UV−vis spectroscopic band of the PIM-1 itself or by tracking the spectral position of the plasmon resonance in gold sensor nanoparticles adjacent to the PIM-1. The optical signals from both methods are directly proportional with each other as well as with the CO$_2$ coverage in the adsorbent, as corroborated by the excellent agreement with first order Langmuir adsorption. Thus, from our optical isothersms we can derive the $Q_a$ of CO$_2$ based on a Clausius−Clapeyron analysis (or the Langmuir adsorption model as shown in the Supporting Information). The average value of $Q_a$ is $\sim$29 kJ/mol and thus in good agreement with the literature as well as with our own control experiment using a volumetric technique.

These results have several key implications. The first one is that, as opposed to the traditionally used gravimetric or volumetric characterization, here we directly measure the adsorbed CO$_2$ on the adsorbent. This eliminates the need to calibrate the sample thickness, mass, and/or volume. The second one is that, for CO$_2$ adsorbents with absorption bands in the UV−vis range, simple UV−vis spectroscopy can be used for adsorption characterization. This fast and low cost method could be particularly well suited for rapid materials screening and complement methods based on infrared spectroscopy. For transparent materials, the plasmonic sensing approach is attractive, because it provides the necessary optical contrast.

In view of the above and the generic nature of our approach, we could be particularly well suited for rapid materials screening for adsorption characterization. This fast and low cost method would enable the experimental investigations with higher resolution. Finally, the PIM-1 corresponds to a signal proportional to the CO$_2$ coverage in the adsorbent, as corroborated by the excellent agreement with our own control experiment using a volumetric adsorption measurement, Langmuir adsorption and thus allows calibration of the sample thickness, mass, and/or volume. The optical signals from both methods are directly proportional with each other as well as with the CO$_2$ coverage in the internal interface between the adsorbent layer and support.


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