Electronic Supplementary Material (ESI) for Nanoscale

Supporting Information

Vapor-liquid equilibrium phase diagrams of the CO_2/methanol, CO_2/ethanol and CO_2/water systems at 45 °C

1. Equations of State

In this work, the Stryjek and Vera modification of the Peng-Robinson equation of state (PRSV-EoS) [1] are applied to represent the VLE of the binary systems involving carbon dioxide, methanol, ethanol and water at 45 °C and different pressures.

PR-EoS is of the form

$$P = \frac{RT}{\mathrm{v} - b} - \frac{a(T)}{\mathrm{v}^2 + 2b\mathrm{v} - b^2} \tag{1}$$

where T, P and v are the temperature, pressure and molar volume. Parameters a and b are given by

$$a_i = 0.457235 \frac{(RT_{ci})^2}{P_{ci}} \left[1 + \kappa_i \left(1 - \sqrt{\frac{T}{T_{ci}}} \right) \right]^2 \tag{2}$$

$$b_i = 0.077796 \frac{RT_{ci}}{P_{ci}} \tag{3}$$

For the PR-EoS, the κ_i term has the form

$$\kappa_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \tag{4}$$

where ω is Pitzer´s acentric factor. For the PRSV-EoS, κ_i is given by

$$\kappa_i = \kappa_{0i} + \kappa_{1i} \left(1 + \sqrt{\frac{T}{T_{ci}}} \right) \left(0.7 - \frac{T}{T_{ci}} \right) \tag{5}$$

with

$$\kappa_{0i} = 0.378893 + 1.4897153\omega_i - 0.17131848\omega_i^2 + 0.0196554\omega_i^3 \tag{6}$$

For mixtures, the Panagiotopoulos-Reid mixing rules are used,

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2} \left[1 - k_{ij} + (k_{ij} - k_{ji}) x_i \right] \tag{7}$$

$$b = \sum_i \sum_j x_i x_j \left(\frac{b_i + b_j}{2} \right) \tag{8}$$

Table 1 gives the pure component parameters, T_{ci}, P_{ci}, ω_i, and k_{1i}.

Table 1. Pure component parameters

Compound	T_c (K)	P_c (MPa)	□ω	k_1
Carbon dioxide	304.21	7.382	0.225	0.04285
Methanol	512.64	8.097	0.565	-0.16816
Ethanol	513.92	6.148	0.644	-0.03374
Water	647.29	22.09	0.344	-0.06635

2. Calculation method

For a multicomponent system, the VLE is obtained equating the fugacities of each component in the vapor phase and in the liquid phases:

$$\begin{aligned} f_i^{\mathrm{V}}(P,T) &= f_i^{\mathrm{L}}(P,T) \\ \varphi_i^{\mathrm{V}} y_i P &= \varphi_i^{\mathrm{L}} x_i P \end{aligned} \tag{9}$$

where φ_i is the fugacity coefficient of component i (1=CO_2), that is easily obtained from the equation of state. For each phase,

$$\sum_{i=1}^{N} y_i = 1; \sum_{i=1}^{N} x_i = 1 \tag{10}$$

where N is the number of components. For the binary systems VLE data were used to correlate the cross interaction parameters k_{ij} and k_{ji}. The Simplex optimization method was used for the parameter regression using the objective function

$$F = \sum_{j=1}^{n} [0.6 \times (x_{1,j}^{\exp} - x_{1,j}^{\text{cal}})^2 + 0.4 \times (y_{1,j}^{\exp} - y_{1,j}^{\text{cal}})^2] \quad (11)$$

where n is the number of the experimental data points. The temperature dependence of the interaction parameters was required because different experimental data were used under various temperatures; typically, they are expressed by linear relationships,

$$k_{ij} = c_{ij} + d_{ij} T \qquad k_{ji} = c_{ji} + d_{ji} T \quad (12)$$

3. Results of the three binaries

Figure 1 compares the calculated VLE data at 45 °C with the parameters listed in Table 2. Figure 1a shows a critical pressure of 10.8 MPa with the CO_2 molar faction of 0.882 for the CO_2(1)/methanol (2) mixture at 45 °C, therefore, the system is supercritical fluid when the pressure is larger than 10.8 MPa and CO_2 molar faction larger than 0.882. Figure 1b also indicates a critical pressure of 10.5 MPa with the CO_2 molar faction of 0.903 for the CO_2/ethanol system at 45 °C , suggesting the system is supercritical fluid when the pressure is larger than 10.5 MPa and CO_2 molar faction larger than 0.903. Yet Figure 1c reveals that the CO_2/water system does not appear supercritical fluid with vapor-liquid two phases at 45 °C and pressures up to 20 MPa.

Table 2. Binary interaction parameters used

System	k_{ij}		k_{ji}	
	c_{ij}	$d_{ij}\times10^4$	c_{ji}	$d_{ji}\times10^4$
CO_2(1)/methanol(2) ††	-0.1776	7.543	0.000002466	2.243
CO_2(1)/ethanol(2) †	-0.02512	4.488	0.003956	2.714
CO_2(1)/water(2)†	-0.4832	12.02	0.1729	1.098

† Binary interaction parameters obtained from [2]; †† Binary interaction parameters correlated with VLE data from [3] (290K-330K).

According to the added CO_2, the estimated molar fractions of CO_2 are 0.92 and 0.89, respectively, for 1ml ethanol and 1ml methanol in a high-pressure

visual vessel (the overall volume is about 12 ml), therefore, for the both cases, the mixtures are in supercritical state as watched by the visual vessel.

Literature Cited

[1] R. Stryjek, J. H. Vera, *Can. J. Chem. Eng.* **1986**, *64*, 323.

[2] J. Li, M. Rodrigues, H. Matos, E. G. de Azevedo, *Ind. Eng. Chem. Res.* **2005**, *44*, 6751.

[3] J. H. Hong, R. Kobayashi, *Fluid Phase Equil.* **1988**, *41*, 269.

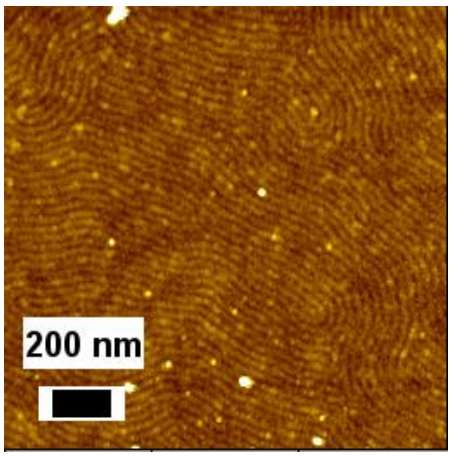


Figure S1. Topographic images of PS-*b*-P4VP thin film spun-cast using toluene and subsequent thermal annealing at 130 °C for 60 h.

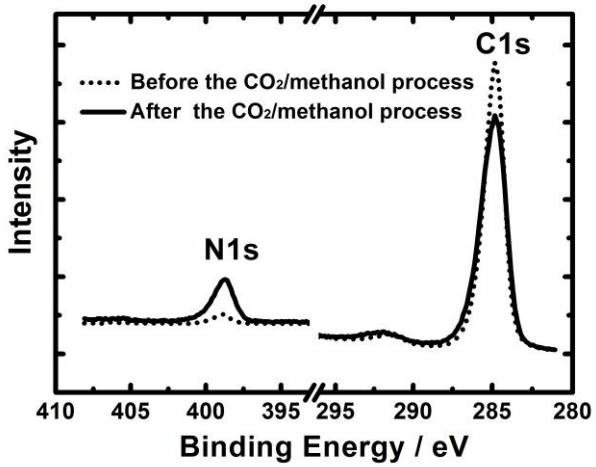
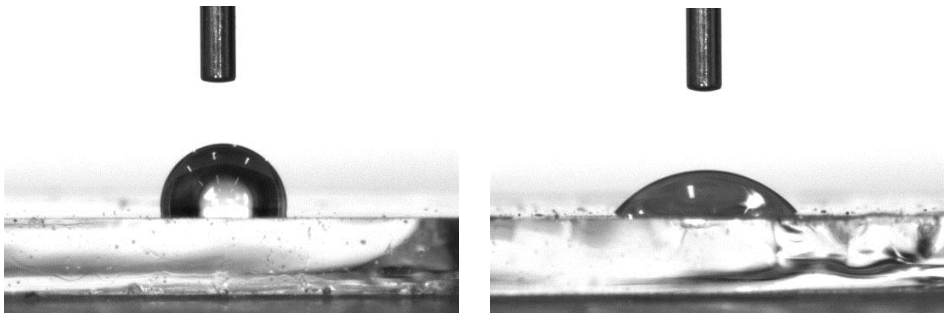


Figure S2. XPS core level scans for C1s and N1s of PS-*b*-P4VP films before (dotted line) and after (solid line) the CO_2/methanol process.



a b

Figure S3. Photographs of water droplets placed on the PS-*b*-P4VP films: (a) the as-cast film (the contact angle = 102.7°); (b) the processed film (the contact angle = 51.2°) at 20 MPa, 45 °C for 0.5 h.

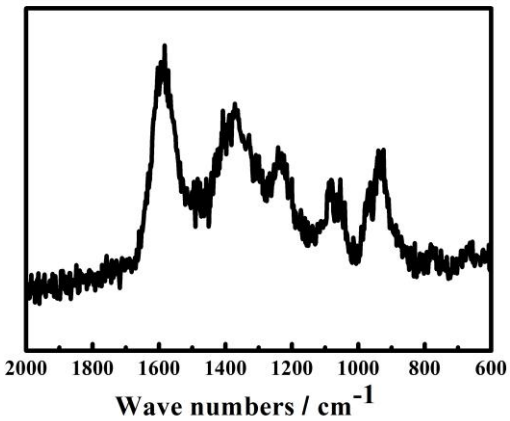


Figure S4. The 638 nm excited Raman spectra of porous PPy film.

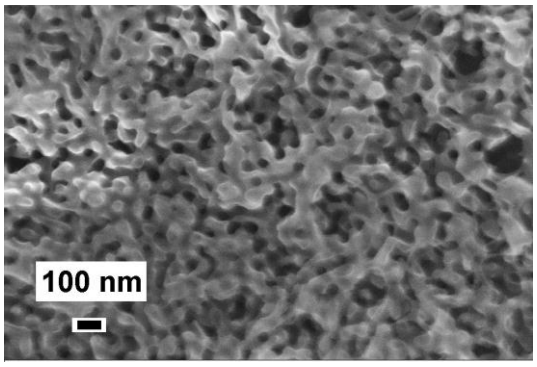


Figure S5. SEM image of a platinum replica of the nanoporous PS-*b*-P4VP film obtained by a CO_2/methanol

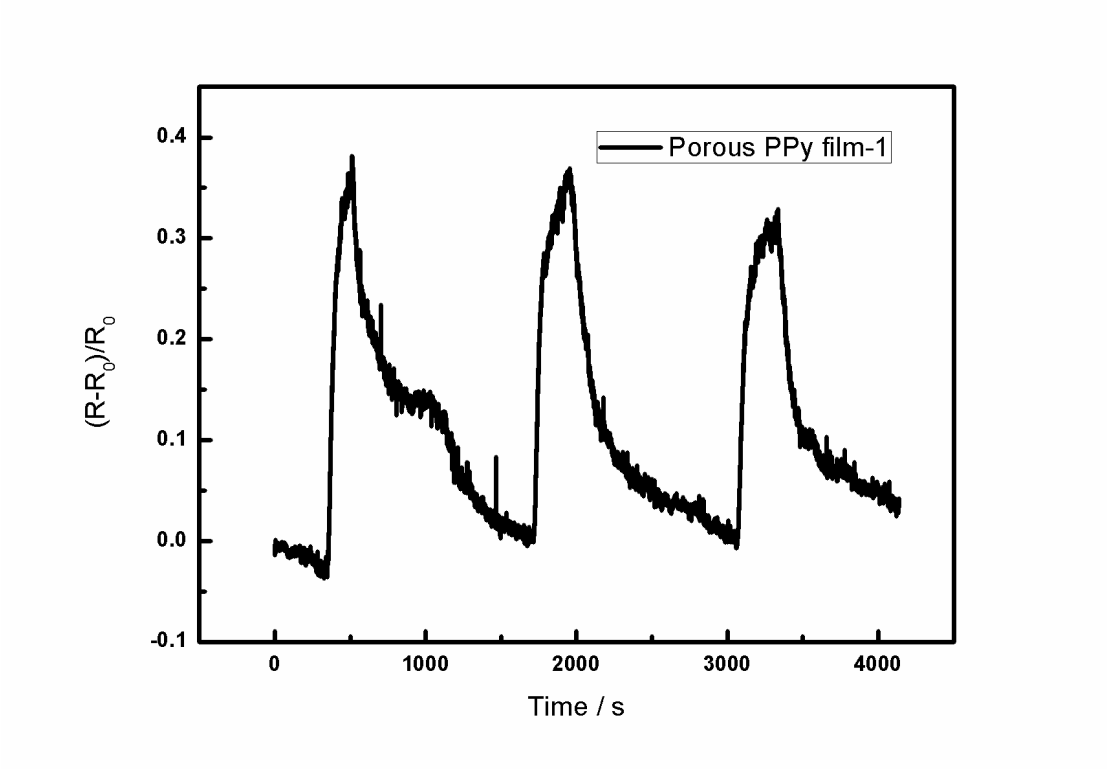


Figure S6. Reversible ammonia gas sensing performance of porous PPy film-1(Sample 1).