Poly(ionic liquid)-Based Nanocomposites and Their Performance in CO₂ Capture

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ABSTRACT: To search for robust CO₂ capture materials, two types of ionic liquids, namely, (p-vinylbenzyl)-trimethylammonium tetrafluoroborate ([VBMTA][BF₄]) and (p-vinylbenzyl)trimethylammonium hexafluorophosphate ([VBMTA][PF₆]), were synthesized and immobilized onto a mesoporous silica (meso-silica) support by the surface-initiated atom-transfer radical polymerization (SI-ATRP) method. The prepared sorbents meso-SiO₂−P[VBMTA][BF₄] and meso-SiO₂−P[VBMTA][PF₆] were well-characterized. Their adsorption behaviors toward CO₂ from simulated flue gases at different pressures were investigated using an adsorption column. Based on a simulated flue gas containing 10 vol % CO₂ at 30 °C, the highest CO₂ adsorption capacity of meso-SiO₂−P[VBMTA][BF₄] was 0.4025 mmol g⁻¹, whereas the corresponding value for meso-SiO₂−P[VBMTA][PF₆] was 0.3793 mmol g⁻¹. Compared with pure poly(ionic liquid)s, the existence of a meso-silica core improves the CO₂ capture capacity. Furthermore, the presence of vapor can improve the CO₂ capture capacity. However, an increase in temperature inhibits the CO₂ capture capacity, implying that the nanocomposites should preferably be used at low temperature.

INTRODUCTION

Currently, the effects of increasing atmospheric carbon dioxide (CO₂) concentrations, which lead to global climate change, have attracted growing attention from researchers worldwide. Not only is the application of CO₂ capture important for environmental issues, but also the removal of CO₂ from gas streams is necessary for some other application areas such as air purification in confined spaces and natural gas treatment. To help achieve the goal of decreasing CO₂ emissions, the synthesis of more efficient organically functionalized materials as CO₂ capture agents has received considerable attention.

Ionic liquids are a type of organic salts that have low melting points and outstanding CO₂ solubilities. Such materials are often utilized as nonvolatile and regenerable carbon dioxide absorbents. Furthermore, they can be grafted onto porous materials to prepare supported liquid membranes. Ionic liquids can endow polymer backbones with ion conducting groups, giving rise to polymers with great stability that can be widely used in material science. In 2005, Tang et al. found that the absorption ability of poly(ionic liquid)s for CO₂ is stronger than that of the corresponding monomers for the first time. Among CRP methods, atom-transfer radical polymerization (ATRP) is a promising and effective method, because it can operate under simple conditions and is suitable for numerous types of monomers. In surface-initiated ATRP, all of the initiator moieties can be immobilized on the surface, so that every polymer chain can form a strong bond with the surface. The published literature indicates that many types of membranes (methacrylate, styrene, etc.) can be grafted successfully by surface-initiated ATRP.

In this work, two types of ionic liquids, namely, (p-vinylbenzyl)trimethylammonium tetrafluoroborate ([VBMTA][BF₄]) and (p-vinylbenzyl)trimethylammonium hexafluorophosphate ([VBMTA][PF₆]), were synthesized and grafted onto a mesoporous silica support by the SI-ATRP method. Meso-SiO₂−P[VBMTA][BF₄] and meso-SiO₂−P-
[VBTMA][PF6] were first characterized using 1H nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). Subsequently, the CO2 capture capacities of meso-SiO2−P−[VBTMA][BF4] and meso-SiO2−P[VBTMA][PF6] were examined systematically. In addition, four factors influencing CO2 capture capacity were investigated. The developed poly(ionic liquid)-based nanocomposites are promising for CO2 capture.

**EXPERIMENTAL SECTION**

**Materials.** Mesoporous nanosilica (mean size, 7.6 nm; pore volume, 1.28 cm3·g−1; surface area, 336 m2·g−1) was dried at 110 °C under a vacuum overnight before use. CuCl [99%,
Sinopharm Chemical Reagent Co., Ltd. (SCRC)] was purified by acetic acid and methanol and dried at 45 °C under a vacuum. (p-Vinylbenzyl)trimethylammonium chloride ([VBTMA][Cl]; 99%, Sigma-Aldrich), N,N,N,N′,N″-pentamethyl diethylenetriamine (PMDETA; 98%, Sigma-Aldrich), 3-aminopropyltriethoxysilane (APTES; 98%, Alfa Aesar), 2-bromoisobutyl bromide (BiBB; 98%, Alfa Aesar), sodium tetrafluoroborate (NaBF4; 99%, Aladdin), ammonium hexafluorophosphate (NH4PF6; 98%, Aladdin), and 2-(trimethylsilyl)ethanol (99%, Aladdin) were used as received. Other materials were used as received from SCRC without further purification.

Synthesis of TMS-EBMP. The detailed preparation of 2-(trimethylsilyl)ethyl 2-bromo-2-methylpropanoate (TMS-EBMP) can be found in our previous publications, and the reaction process is shown in Scheme 1a.

Synthesis of [VBTMA][BF4] and [VBTMA][PF6]. [VBTMA][BF4] was prepared according to the published method, and [VBTMA][PF6] was prepared using ammonium halide by an ion-exchange reaction, as shown in Scheme 1b. First, CH3CN (15 mL), NH4PF6 (2.15 g, 0.0132 mol), and [VBTMA][Cl] (2.54 g, 0.012 mol) were placed in a flask. Then, similarly to the synthesis of [VBTMA][BF4], white crystals of [VBTMA][PF6] were obtained prior to cryopreservation under sealed conditions. 1H NMR for [VBTMA][PF6]: δ 2.96 (s, 9H), 5.38 (d, 1H), 5.96 (d, 1H), 6.81 (q, 1H), 7.50 (d, 2H), 7.61 (d, 2H). 

Synthesis of P[VBTMA]−P[VBTMA][PF6] Nanocomposites. The synthesis process for meso-SiO2−Br was the same as in our previous work and as in Scheme 1c. First, CH3CN (15 mL), NH4PF6 (2.15 g, 0.0132 mol), and [VBTMA][Cl] (2.54 g, 0.012 mol) were placed in a flask. Then, similarly to the synthesis of [VBTMA][BF4], white crystals of [VBTMA][PF6] were obtained prior to cryopreservation under sealed conditions. 1H NMR for [VBTMA][PF6]: δ 3.02 (s, 9H), 5.38 (d, 1H), 5.96 (d, 1H), 6.81 (q, 1H), 7.50 (d, 2H), 7.61 (d, 2H). 

Measurements. 1H nuclear magnetic resonance spectra were measured using a Bruker Advance II 400 MHz instrument and deuterated dimethyl sulfoxide (DMSO-d6) as the solvent. Melting points were detected on a X-4 digital display microscopic melting point meter calibrated by anaculide (melting point = 114 °C).

Fourier transform infrared (FT-IR) spectra were recorded using Nicolet Avatar 330 FT-IR spectrophotometer in transmission mode.

Elemental analysis (EA) was performed on a Vario EL III elemental analyzer.

X-ray photoelectron spectroscopy (XPS) analysis was carried out using a PHI Quantum 2000 scanning electron spectroscopy (ESCA) microprobe. The exciting source was Al Kα1,2 radiation with a binding energy of 1486.60 eV and a voltage of 15 kV in constant-analyzer-energy (CAE) mode, and the energy was calibrated at C 1s = 284.8 eV.

Thermogravimetric analysis (TGA) was performed on an SDTQ 600 instrument from room temperature to 800 °C under a nitrogen atmosphere at a 10 °C·min⁻¹ heating rate.

Scanning electron microscopy (SEM) observations were made on a Hitachi S-4800 microscope at an acceleration voltage of 10 kV. The samples were prepared as follows: A 0.2 mg·mL⁻¹ ethanol solution of meso-silica and meso-SiO2−Br and a 0.2 mg·mL⁻¹ DMF solution of meso-SiO2−[P[VBTMA]−[BF4]] and meso-SiO2−2[P[VBTMA][PF6]] were mounted onto silicon wafers and dried at room temperature.

The CO2 capture capacity was measured on a CO2 adsorption system that mainly consisted of adsorbed gas, purge gas, fixed adsorber, flow and pressure regulating system, and a gas concentration analysis system (Scheme 2). The adsorption column filled with 1.5 g of adsorbent was placed in a temperature-controlled tubular furnace. CO2 was blended with nitrogen (99.999%). Gas chromatography (GC) was used to detect the CO2 concentration. Adsorbents were treated under a nitrogen flow of 50 mL·min⁻¹ at 150 °C for 90 min and then cooled to 30 °C. After that, the nitrogen flow was switched to a CO2-containing simulated flue gas at 50 cm³·min⁻¹, which kept the mole fraction of CO2 at 0.1 at atmospheric pressure.

**RESULTS AND DISCUSSION**

Characterization of SiO2−P[VBTMA][BF4] and SiO2−2[P[VBTMA][PF6]] Nanocomposites. Using the trimethylsilyl-(TMS)-labeled “sacrificial initiator” method, the obtained macromolecules in solution served as a reference substance for the polymers formed on the surface. Thus, the molecular weight and polydispersity of the grafted polymer could be analyzed by size-exclusion chromatography (SEC) of the polymer obtained in solution. However, because the charged groups existing in the polyionic material could lead to a complicated and unreliable molecular weight, it is difficult to characterize such materials by SEC. Herein, the monomer...
conversion was obtained through a gravimetric method, and the number-average molecular weights ($M_{\text{n,NMR}}$) of the precipitated TMS–P[VBTMA][BF$_4$] and TMS–P[VBTMA][PF$_6$] were calculated from $^1$H NMR spectra by the trimethylsilyl-(TMS-) labeled sacrificial initiator method. The detailed calculation process was presented in our previous work.$^{42}$ The $^1$H NMR spectra of the resultant polymers and the kinetics of ATRP are shown in Figure 1. As depicted in Figure 1a, the two signals present at 7.1 and 6.5 ppm correspond to the benzene ring group. The signal at 4.3 ppm is attributed to methylene belonging to a benzene ring. The signal at 2.9 ppm corresponds to methyl groups attached to a nitrogen atom. The broad peak at 1.5 ppm originates from the methane and methine protons of the main chain. The characteristic signal of TMS-labeled initiator is located at 0.0 ppm and was used to calculate the degree of polymerization. In addition, the linearity of the kinetic plot (Figure 1b) demonstrates the constant number of active species in the two systems. At the end of polymerization, the conversions of the [VBTMA][BF$_4$] and [VBTMA][PF$_6$] systems were about 53% and 54%, respectively. Clearly, the two monomers have similar polymerization rates. The evolution of $M_{\text{n,NMR}}$ (Figure 1c) also increased linearly as polymerization proceeded, and the two poly(ionic liquids) had similar degrees of polymerization after predetermined polymerization times (Figure 1b). Because of the different molecular weights of the monomers, $M_n$ for TMS–P[VBTMA][BF$_4$] was 17775 g·mol$^{-1}$, and $M_n$ for TMS–P[VBTMA][PF$_6$] was 14378 g·mol$^{-1}$. These results demonstrate the classical features of ATRP.

Core–shell meso-SiO$_2$–P[VBTMA][BF$_4$] and meso-SiO$_2$–P[VBTMA][PF$_6$] were synthesized by SI-ATRP (Scheme 1d). The FT-IR spectra of the products are presented in Figure 2.

![Figure 1](image1.png)  
**Figure 1.** Experimental data for TMS–P[VBTMA][BF$_4$] and TMS–P[VBTMA][PF$_6$]: (a) $^1$H NMR spectra, (b) semilogarithmic kinetic plot and monomer conversion vs polymerization time, (c) molecular weight ($M_{\text{n,NMR}}$) vs monomer conversion.

![Figure 2](image2.png)  
**Figure 2.** FT-IR spectra of (a) meso-SiO$_2$–Br, (b) meso-SiO$_2$–P[VBTMA][BF$_4$], and (c) meso-SiO$_2$–P[VBTMA][PF$_6$].

For meso-SiO$_2$–Br (Figure 2a), the signals at 1109 and 470 cm$^{-1}$ originated from tetrahedral silica structures. The signal for Si–O–Si bending can be found at 800 cm$^{-1}$. In addition, the presence of amide groups (N–H bending) could be verified by the peak at 1573 cm$^{-1}$. The CH$_3$ stretching and bending vibration was confirmed by signals at 1383 and 2931 cm$^{-1}$. In the FT-IR spectrum of meso-SiO$_2$–P[VBTMA][BF$_4$] (Figure 2b), the characteristic peaks of both the meso-SiO$_2$ core and the P[VBTMA][BF$_4$] shell are included. The peaks for C–H bending vibration are located at 807 and 841 cm$^{-1}$, whereas that for the benzene ring in P[VBTMA][BF$_4$] is located at 1418 and 1485 cm$^{-1}$. In particular, the peak at 1030 cm$^{-1}$ belonging to B–F stretching vibrations indicates that the surface of the nanosilica particles was successfully grafted with P[VBTMA][BF$_4$]. Similarly, in the FT-IR spectrum of meso-SiO$_2$–P[VBTMA][PF$_6$] (Figure 2c), characteristic peaks were also observed, and the signal for the P–F stretching vibration at 842 cm$^{-1}$ verified that P[VBTMA][PF$_6$] was also successfully grafted.
Additionally, the elemental contents of meso-SiO$_2$−P[VBTMA][BF$_4$] and meso-SiO$_2$−P[VBTMA][PF$_6$] were obtained by EA as summarized in Table 1. For meso-SiO$_2$−P[VBTMA][BF$_4$], the EA data show the following contents: N, 4.99%; H, 6.69%; C, 51.53%. The values calculated from the molecular formula of the corresponding monomer [VBTMA][BF$_4$] are N, 5.32%; H, 6.90%; C, 54.78%. For meso-SiO$_2$−P[VBTMA][PF$_6$], the EA data indicate the following contents: N, 4.42%; H, 5.54%; C, 42.32%. The values calculated from the molecular formula of [VBTMA][PF$_6$] are N, 4.36%; H, 5.65%; C, 44.87%. Generally speaking, the elemental contents in the nanocomposites decreased only slightly in comparison to those in the monomer, which might be the result of the immobilization of the initiator onto meso-SiO$_2$ in the nanocomposite. Furthermore, the uncertainty during testing and software measurement deviations could also cause differences, which might be the reason the EA value is much greater than the calculated value for the N content in meso-SiO$_2$−P[VBTMA][PF$_6$]. However, the deviations of all the detected elemental contents were within the error allowance, and the data still indicate that the SI-ATRP was successful.

Table 1. EA and Calculated Elemental Contents

<table>
<thead>
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<th>material</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>meso-SiO$_2$−P[VBTMA][BF$_4$]</td>
<td>51.53</td>
<td>6.69</td>
<td>4.99</td>
</tr>
<tr>
<td>[VBTMA][BF$_4$]</td>
<td>54.78</td>
<td>6.90</td>
<td>5.32</td>
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<tr>
<td>meso-SiO$_2$−P[VBTMA][PF$_6$]</td>
<td>42.32</td>
<td>5.54</td>
<td>4.42</td>
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<tr>
<td>[VBTMA][PF$_6$]</td>
<td>44.87</td>
<td>5.65</td>
<td>4.36</td>
</tr>
</tbody>
</table>

*Average of two EA results. Calculated from the corresponding molecular formula.

P[VBTMA][BF$_4$], the EA data show the following contents: N, 4.99%; H, 6.69%; C, 51.53%. The values calculated from the molecular formula of the corresponding monomer [VBTMA][BF$_4$] are N, 5.32%; H, 6.90%; C, 54.78%. For meso-SiO$_2$−P[VBTMA][PF$_6$], the EA data indicate the following contents: N, 4.42%; H, 5.54%; C, 42.32%. The values calculated from the molecular formula of [VBTMA][PF$_6$] are N, 4.36%; H, 5.65%; C, 44.87%. Generally speaking, the elemental contents in the nanocomposites decreased only slightly in comparison to those in the monomer, which might be the result of the immobilization of the initiator onto meso-SiO$_2$ in the nanocomposite. Furthermore, the uncertainty during testing and software measurement deviations could also cause differences, which might be the reason the EA value is much greater than the calculated value for the N content in meso-SiO$_2$−P[VBTMA][PF$_6$]. However, the deviations of all the detected elemental contents were within the error allowance, and the data still indicate that the SI-ATRP was successful.

XPS spectra were also obtained to verify the successful immobilization of P[VBTMA][BF$_4$] and P[VBTMA][PF$_6$]. The F 1s, N 1s, and B 1s spectra of the meso-SiO$_2$−P[VBTMA][BF$_4$] surface are shown in Figure 3 to confirm the structure. In Figure 3b, the F 1s, N 1s, and B 1s signals are located at 686.0, 402.6, and 194.1 eV, respectively. The N 1s peak at 402.6 eV belongs to the nitrogen atom (N$^+$) of the [VBTMA] cation. The XPS survey spectra of F 1s (686.5 eV), N 1s (402.6 eV), and P 2p (136.6 eV) for the P[VBTMA][PF$_6$] shell on the silica surface can be found in Figure 4.

Thermal Properties. The TGA curves of meso-SiO$_2$−Br, meso-SiO$_2$−P[VBTMA][BF$_4$], and meso-SiO$_2$−P[VBTMA][PF$_6$] are displayed in Figure 5. Corresponding to its higher $M_n$ value, meso-SiO$_2$−P[VBTMA][BF$_4$] has a higher weight loss than meso-SiO$_2$−P[VBTMA][BF$_4$] involving similar monomer units, which is caused by the cleavage of the polymer backbone, namely, carbonation. The organic components present in the products result in the weight losses shown in the TGA curves of meso-SiO$_2$−Br, meso-SiO$_2$−P[VBTMA][BF$_4$], and meso-SiO$_2$−P[VBTMA][PF$_6$]. Before thermal decomposition, there is a small quantity of weight loss in the three curves, which might be because of the evaporation of physically adsorbed water. Because of the greater hydrophilicity of the P[VBTMA][BF$_4$] shell, this phenomenon was much more obvious for meso-SiO$_2$−P[VBTMA][BF$_4$]. It can be seen that the residual weights for meso-SiO$_2$−P[VBTMA][BF$_4$] and meso-SiO$_2$−P[VBTMA][PF$_6$] were 25.6% and 13.0%, respectively, at 750 °C. The decomposition temperatures of meso-SiO$_2$−P[VBTMA][BF$_4$] and meso-SiO$_2$−P[VBTMA][PF$_6$] both exceed 300 °C, implying that they both exhibit excellent thermal stability.
Morphology of Mesoporous Nanocomposites. The morphologies and dispersions of meso-SiO$_2$−Br, meso-SiO$_2$−P[VBTMA][BF$_4$], and meso-SiO$_2$−P[VBTMA][PF$_6$] were observed by SEM (Figure 6). Marked differences in the particle sizes of meso-SiO$_2$−Br particles, meso-SiO$_2$−P[VBTMA][BF$_4$] nanocomposite, and meso-SiO$_2$−P[VBTMA][PF$_6$] nanocomposite were found. With the poly(ionic liquid)s grafting onto the surface of meso-silica, the particle size increased, whereas the dispersion state seemed to remain basically the same. Because of the high surface energy of SiO$_2$, the composites aggregated together. These differences in morphology are expected to lead to different performance characteristics, including different CO$_2$ capture capacities.

CO$_2$ Capture Capacity. The adsorption capacity of an adsorbent for CO$_2$ can be calculated as

$$q = \frac{1}{M} \int_0^t Q \frac{C_0 - C}{1 - C} \frac{dt}{T_0 V_m}$$

where $q$ is the adsorption capacity of the adsorbent for CO$_2$ (mmol·g$^{-1}$); $M$ is the mass of adsorbent (g); $Q$ is the gas flow rate (mL·min$^{-1}$); $C_0$ and $C$ are the influent and effluent CO$_2$ volume concentrations, respectively (%); $t$ represents the time (min); $T_0$ is 273.15 K; $T$ represents the gas temperature (K); and $V_m$ is 22.4 mL·mmol$^{-1}$.

The CO$_2$ adsorption kinetics of the nanocomposites are shown in Figure 7. The two adsorbents can reach adsorption equilibrium quickly in about 5 min. They take up 0.4025 and 0.3793 mmol of CO$_2$ per gram, respectively, based on an average of three measured results at equilibrium, as calculated using eq 1. According to Tang et al.’s work on the adsorption capacity shown as mole percentages of monomer units,$^{30}$ the CO$_2$ sorption capacities of P[VBTMA][BF$_4$] and P[VBTMA][PF$_6$] involved in the nanocomposites were 0.3884 and 0.3323 mmol·g$^{-1}$, respectively. To some extent, these results show the advantage of poly(ionic liquid)-based nanocomposites. Although the data on the advantage of nanocomposites are not obvious, this might be the result of the method utilized in the work. In this work, we assumed that the degree of polymerization from meso-silicon initiator in nanocomposites was the same as that for the pure poly(ionic liquid)s initiated by TMS-labeled initiator. Actually, because of the steric hindrance effect of SiO$_2$, the reaction rates might differ from each other, with the polymerization of monomer using the TMS-labeled initiator proceeding faster than that of the monomer grafted on the meso-SiO$_2$, as confirmed by our group through a simulation study.$^{43}$ Thus, the effective sorption part in the nanocomposites would be less than that in pure poly(ionic liquid)s. Even so, the results still showed that the nanocomposites had better sorption abilities. The improvements should result from the introduction of meso-silica into the nanocomposites. Although both the core and the shell of the nanocomposites have certain capacities, some pores will inevitably be filled by polymer chains, and thus, the capacity of the nanocomposites will be lower than the sum of the capacities of the two single components.

The adsorption isotherms of meso-SiO$_2$−P[VBTMA][BF$_4$] and meso-SiO$_2$−P[VBTMA][PF$_6$] at various CO$_2$ pressures and 30 °C are shown in Figure 8. Obviously, $q$ increases as the pressure increases. Although the adsorption isotherm of meso-SiO$_2$−P[VBTMA][BF$_4$] appears to be nonlinear, that of meso-SiO$_2$−P[VBTMA][PF$_6$] is almost linear. The Henry’s constant can be calculated as

$$H_i = \lim_{x_i \to 0} \frac{P}{x_i}$$

Figure 6. SEM images of (a) meso-SiO$_2$−Br, (b) meso-SiO$_2$−P[VBTMA][BF$_4$], and (c) meso-SiO$_2$−P[VBTMA][PF$_6$].

Figure 7. CO$_2$ adsorption kinetics of (a) meso-SiO$_2$−P[VBTMA][BF$_4$] and (b) meso-SiO$_2$−P[VBTMA][PF$_6$].
where $H_i$ is the Henry’s constant, $x_i$ is the mole fraction of gas in the adsorbent, and $P_i$ is the CO$_2$ pressure.

Because of the nonlinearity of $x_i$ versus $P_i$ throughout the whole pressure range, one can fit the data and extrapolate the slope to zero CO$_2$ partial pressure when calculating $H_i$. The computed $H_i$ values at 30 °C are 2.35 and 6.48 bar for meso-SiO$_2$−P[VBTMA][BF$_4$] and meso-SiO$_2$−P[VBTMA][PF$_6$], respectively, which are at the same level as those of ammonium-based poly(ionic liquid)s at 295 K. $^{21}$

**Factors Influencing CO$_2$ Capture Capacity.** In consideration of the advantage of meso-SiO$_2$−P[VBTMA][BF$_4$] in CO$_2$ capture and experimental efficiency, we examined the dynamic adsorption process to obtain the adsorption data and trend. As shown in Figure 9, the core consisting of silica, the shell consisting of poly(ionic liquid), the presence of water vapor, and the test temperature all had an impact on the capacity of the nanocomposite adsorbents. From Figure 9a, one can see that the mesoporous silica core endows the mesoporous nanocomposite with a higher capacity than common nanocomposites, which also testifies to the existence of porous structures. The stereostructure and high surface area of meso-silica supply the high grafting density of the nanocomposite and are also beneficial for the diffusion of CO$_2$ into the nanocomposites. $^{45}$ Additionally, mesoporous nanocomposites with different shells result in different capacities, according to Figure 9b. We surmise that the difference is caused by the different anion diameters and their physical and chemical properties. The presence of water vapor can improve the CO$_2$ capture capacity, as shown in Figure 9c, which can be explained by the partial production of bicarbonate during CO$_2$ adsorption.

![Figure 8](image1.png)

**Figure 8.** Isothermal adsorption of CO$_2$ by meso-SiO$_2$−P[VBTMA][BF$_4$] and meso-SiO$_2$−P[VBTMA][PF$_6$] at different pressures.

![Figure 9](image2.png)

**Figure 9.** CO$_2$ adsorption in nanocomposites with different (a) cores, (b) shells, and (c) pretreatments and (d) CO$_2$ adsorption data of meso-SiO$_2$−P[VBTMA][BF$_4$] at different temperatures.
on nanocomposites with hydrophilic ionic liquid monomers ([VBTMA][BF₄]) under humid conditions. However, the increase of q is not evident at the beginning, which might be because of the close distance which is too short that the bicarbonate formation reaction could not reach equilibrium. Therefore, the dry adsorbent has a real capacity, whereas the wet adsorbent shows an apparent sorption quantity that is higher than the former. Finally, the impact of pressure was investigated. As shown in Figure 9d, at a certain temperature, the capacity increased as the pressure increased. In contrast, at a certain pressure, the capacity decreased as the temperature increased, because adsorption is an exothermic process, so it is not beneficial to perform adsorption at high temperatures, and also, the movement of molecules becomes vigorous, which is not good for the adsorption process. The equilibrium times for the five selected temperatures were almost the same, indicating that the temperature influences the capacity, but not the equilibrium time. The above data show that low temperatures are preferable for the use of the nanocomposites prepared in this work.

As a whole, the above data and analysis can provide a possible explanation for the adsorption phenomenon: Absorption (occurring in the bulk) and adsorption (occurring at the surface) both take place during CO₂ adsorption on the polymer shell. Subsequently, because of the driving force of a concentration difference, CO₂ diffuses into the pores of the host silica core, causing secondary adsorption. The CO₂ adsorption cycle of meso-SiO₂−P[VBTMA][BF₄] is shown in Figure 10. By comparing the different cycles, it can be seen that irreversible chemical absorption occurs during the sorption process, which leads to a capacity decrease at the second cycle. However, the main process is still physical adsorption, which enables the material to be used repeatedly. In addition, for the purpose of improving the adsorption capacity of the polymers, it is important to avoid filling polymers into the pores of the meso-silica.

**CONCLUSIONS**

Two nanocomposite absorbents, namely, meso-SiO₂−P[VBTMA][BF₄] and meso-SiO₂−P[VBTMA][PF₆], were synthesized by SI-ATRP using mesoporous nanosilica as the initiator. Their CO₂ adsorption behaviors were investigated under different conditions. The adsorbents were still porous and had reasonably high surface areas after ionic liquid monomer had been grafted onto the meso-silica; therefore, they could adsorb CO₂ rapidly and show outstanding adsorption capacities and selectivities, as well as repeatability. At 30 °C, meso-SiO₂−P[VBTMA][BF₄] had the highest CO₂ absorption capacity of 0.4025 mmol g⁻¹, whereas meso-SiO₂−P[VBTMA][PF₆] showed the highest CO₂ absorption capacity of 0.3793 mmol g⁻¹ for a simulated flue gas containing 10 vol % CO₂. Compared with pure poly(ionic liquid)s, the presence of the meso-silica core does enhance the CO₂ capture capacity. The presence of water vapor can strengthen the CO₂ capture capacity, which is why meso-SiO₂−P[VBTMA][BF₄] with a hydrophilic shell was found to have a higher capacity than meso-SiO₂−P[VBTMA][PF₆]. Increasing the test temperature inhibited the CO₂ capture capacity, which implies that low temperatures are preferable for the use of the nanocomposites. Overall, the introduction of meso-silica not only increases the capacity of the polymer but also decreases the cost, which is promising for applications in CO₂ capture.

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H.C. and P.W. contributed equally to this work.

**Notes**

The authors declare no competing financial interest.

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**Figure 10.** CO₂ adsorption cycle of meso-SiO₂−P[VBTMA][BF₄].


