Probing Porosity and Pore Interconnectivity in Self-Assembled TiO$_2$–Graphene Hybrid Nanostructures Using Hyperpolarized $^{129}$Xe NMR

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ABSTRACT:

Hyperpolarized (HP) $^{129}$Xe NMR was used to probe the porosity and interconnectivity of pores in self-assembled hybrid TiO$_2$–graphene nanostructures. We have demonstrated that HP $^{129}$Xe NMR is a powerful technique in probing any changes in porosity and interconnectivity of the pores caused by the addition of a small amount of functionalized graphene sheets (FGGs) (1% weight percent) into the network of mesoporous TiO$_2$. To obtain the information on the changes in porosity and interconnectivity of the pores caused by the addition of a small amount of FGGs, a comparative study has been carried out by acquiring HP $^{129}$Xe NMR spectra under identical experimental conditions for both pure mesoporous TiO$_2$ and hybrid TiO$_2$–FGGs. The HP $^{129}$Xe NMR results from our comparative study suggest that TiO$_2$ and graphene are mixed uniformly on the nanoscale and the resulting hybrid nanostructure has better channel connectivity between different domains, enhancing the transport property for Li-insertion/extraction.

INTRODUCTION

There has been increased interest in developing hybrid nanostructured materials with controlled porosity for electrochemical energy storage and other energy related applications. The extent of interconnectivity between nano- or mesopore domains in such materials markedly affects their transport properties. Therefore, characterization of resident porosity and pore interconnectivity is key to better understanding ion transport mechanisms in nanoporous materials.

The pore geometry in most porous materials, even in ordered mesoporous silica, is complex and is exemplified by interconnected cages, channels, and micropores.1 As a result of these complex topologies and buried interfacial structures, characterization of pore interconnectivity in nano- or mesoporous materials is often challenging and mandates application of several characterization methods. The most common techniques such as small-angle X-ray or neutron scattering, and gas absorption, however, do not provide direct information on how channels and cages are connected.

Over the years, $^{129}$Xe NMR has developed into a powerful and robust method for probing the void structure in extremely high surface area porous solids.2–5 The large chemical shift range of $^{129}$Xe is strongly dependent on both local environmental and chemical factors such as the composition of the matrix, nature and concentration of coadsorbed molecules, and the shape and size of inherent void spaces.2–5 The use of optical pumping approaches for the production of hyperpolarized (HP) xenon permits a dramatic increase in the sensitivity of $^{129}$Xe NMR up to a factor of $10^4$, thereby enabling these pore characterization studies. Using HP xenon produced under continuous flow (CF)

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conditions, measurements are possible at very low xenon concentration, which minimizes the contribution from Xe—Xe interactions to the observed chemical shift. As such, the observed $^{129}$Xe chemical shifts can be assigned principally to interactions between the xenon atoms and the porous surfaces. Because spin-polarized Xe gas percolates through the interconnected pores and samples the local pore environments, HP $^{129}$Xe NMR has the unique advantage of directly probing not only these buried interfaces but also the interconnectivity between the pores.

$\text{TiO}_2$ has been extensively studied to understand correlations between nanostructure and charge migration through the structure. The $^{129}$Xe NMR data can provide insights into the charge migration pathways within the nanoscale structure. The observed chemical shift can be related to the charge density and the local electrostatic environment around the $^{129}$Xe atom. High-resolution $^{129}$Xe NMR can be used to probe the local environment of the $^{129}$Xe atom, which can provide information about the nature of the interactions between the xenon atoms and the surrounding electrostatic environment.

To further increase the Li ion insertion rate and capacity, a nanostructured $\text{TiO}_2$—graphene hybrid material has been prepared by means of an anionic surfactant mediated self-assembly process described in our recent paper. Graphene is a two-dimensional macromolecular sheet of carbon atoms with a honeycomb structure that exhibits excellent electronic conductivity and mechanical stability. Hybrid materials synthesized here showed significantly enhanced Li ion insertion/extraction in $\text{TiO}_2$. The specific capacity more than doubled at high charge rate, as compared to the pure $\text{TiO}_2$ phase, indicating that incorporation of these conducting graphene sheets has the potential to markedly improve the performance of Li ion battery electrode materials.

In this Article, variable-temperature HP $^{129}$Xe NMR spectroscopy is applied to probe the porosity and interconnectivity of self-assembled $\text{TiO}_2$—FGSs (functionalized graphene sheets) hybrids. Results obtained for hybrid $\text{TiO}_2$—FGSs are compared to those for single phase mesoporous $\text{TiO}_2$. Our HP $^{129}$Xe NMR study addresses several important issues including FGSs insertion into the network of mesoporous $\text{TiO}_2$, uniformity of $\text{TiO}_2$/FGSs mixtures at the nanoscale, and fluctuations in porosity and interconnectivity of pores in $\text{TiO}_2$ nanostructures caused by addition of FGSs into the mesoporous $\text{TiO}_2$ network. Such information is critical for understanding the role of graphene in Li ion insertion/extraction kinetics.

## EXPERIMENTAL SECTION

### Materials Synthesis and Characterization

Three types of materials were used in HP $^{129}$Xe NMR measurements. XRD, TEM, and XPS were used for characterizing these materials. XRD patterns were obtained on a Philips Xpert X-ray diffractometer using Cu Kα radiation at $\lambda = 1.54$ Å. The TEM imaging was performed on a JEOL JSM-2010 TEM operated at 200 kV. XPS characterization was performed using a Physical Electronics Quantum 2000 scanning ESCA microprobe with a focused monochromatic Al Kα X-ray (1486.7 eV) source and a spherical section analyzer.

Functionalized graphene sheets (FGSs) used in this study were prepared by means of thermal expansion of graphite oxide. In comparison to the graphene produced by the chemical reduction of graphite oxide, graphene prepared by the thermal expansion approach can have tunable C/O ratios ranging from 10 to 500, and thus its ionic conductivity can be tuned to higher values. FGSs processing begins with chemical oxidation of graphite flakes to increase the $c$ axis spacing from 0.34 to 0.7 nm as described elsewhere. The resultant graphite oxide is then split by a rapid thermal expansion to yield separated graphene sheets. X-ray photoemission spectroscopy (XPS) of FGSs shows a single sharp C1s peak at a binding energy of 284.6 eV, indicating a high degree of sp$^2$ conjugation. A small shoulder at 286 eV indicates the existence of some C—O bonds corresponding to the epoxy and hydroxyl functional groups on the FGSs.

Mesoporous crystalline $\text{TiO}_2$ was prepared according to a previous report using a one-step low-temperature crystallization approach. In a typical synthesis, 1.2 mL of 0.5 M sodium dodecyl sulfate ($\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$) (SDS) solution (0.6 mmol) was added into 10 mL of 0.12 M TiCl$_3$ solution (1.2 mmol) under vigorous stirring. Subsequently, 0.8 mL of 1.0 wt % $\text{H}_2\text{O}_2$ solution (0.26 mmol) was added dropwise under vigorous stirring. The mixture was then diluted to a total volume of 55 mL by adding deionized water and further stirred in a polypropylene flask at 60 °C for 15 h. The precipitates were separated by centrifuge followed by washing with deionized water and ethanol. Next, the product was dried in a vacuum oven at 60 °C overnight and subsequently calcined in static air at 400 °C for 2 h.

The functionalized hybrid $\text{TiO}_2$—FGSs were also prepared using a one-step low temperature self-assembly route similar to that for the synthesis of mesoporous $\text{TiO}_2$. A mild, low-temperature (below 100 °C) crystallization process was carried out to form crystalline $\text{TiO}_2$ having a controlled crystalline phase (i.e., rutile or anatase) on the graphene sheets. The low temperature condition was also important in preventing aggregation of graphene sheets at elevated temperatures. In line with our previous studies using a low-temperature oxidative hydrolysis and crystallization process, rutile-phase $\text{TiO}_2$—FGSs is obtained containing a minor anatase phase.

In a typical preparation of rutile $\text{TiO}_2$—FGSs hybrid materials (e.g., 1 wt % FGSs), 4.8 mg of FGSs and 3 mL of SDS aqueous solution (0.5 mol/L) were mixed together. The mixture was diluted to 15 mL and sonicated for 10—15 min (Branson Sonifier S-450A, 400 W). A 25 mL portion of TiCl$_3$ (0.12 mol/L)
aqueous solution was added to as-prepared SDS–FGS dispersions while stirring. Next, 2.5 mL of H2O2 (1 wt %) was added dropwise followed by deionized water under vigorous stirring until a total volume of 80 mL was achieved. All resulting mixtures were further stirred in a sealed polypropylene flask at 90 °C for 16 h. The precipitates were separated by centrifugation followed by washing with deionized water and ethanol. The centrifuging and washing processes were repeated three times. The product was then dried in a vacuum oven at 70 °C overnight and subsequently calcined in ambient air at 400 °C for 2 h. The thermal gravimetric analysis (TGA) indicated an approximate 50 wt % loss of FGSs following calcination in air at 400 °C for 2 h.

**HP 129Xe NMR Measurements.** HP 129Xe NMR experiments were carried out on a Chemagnetics spectrometer operating at 82.98 MHz (magnetic field 7.05 T) using a specially designed variable-temperature double-resonance magic angle spinning (MAS) probe with a continuous flow (CF) of HP xenon. For 129Xe NMR experiments, a single-pulse (SP) Bloch-decay method was used, and samples were loaded into 7.5 mm Zirconia PENCIL rotors. The 129Xe NMR experiments were performed with nonspinning SP spectra were collected with a 4,5 μs (90°) 129Xe pulse and a repetition delay of 1 s. The number of transients was 100.

In collaboration with Prof. Brian Saam’s group at university of Utah, we have recently designed and constructed a highly efficient HP Xe 129Xe polarizer that provided probe nuclei for this investigation. This Xe polarizer has a unique design and is based upon a report by the Hersman group.37 Unlike most of the HP xenon polarizers available in other laboratories, a low-pressure environment is used in this design to mitigate quenching efficient transfer of spin from the excited Rb electron manifold to the Xe nucleus. Effective use of the pump diode laser power (80 W) at 795 nm is provided by means of a long path-length cell (1 m), high Rb vapor density, and by counter flowing the spin exchanged optically pumped (SEOP) gas in a direction opposite to that of the laser propagation direction. This unique arrangement achieves a remarkably high polarization rate (>35%), even at high flow velocity. With this enhanced sensitivity, our new 129Xe NMR polarizer will enable future studies of materials having relatively low surface area such as thin porous membranes and self-assembled structures in solution.

A xenon—helium—nitrogen mixture with a volume composition of 1%—66%—33% was used in all CF HP experiments. The flow rate was kept constant in the range of about 500 scce/min (gas flow normalized to standard conditions). In CF HP experiments, the HP xenon flow was delivered directly from the polarizer to the coil region of the NMR probe through a 1.5 mm ID plastic tubing. Variable-temperature NMR experiments in the 183–333 K range were performed using a PNNL-designed cell and temperature controller. The temperature inside the NMR coil of the CF probe was calibrated using the 207Pb resonance in Pb(NO3)2.38 All measured 129Xe NMR chemical shift data were referenced to the xenon gas chemical shift extrapolated to zero pressure (0 ppm).

**RESULTS AND DISCUSSION**

Detailed characterization of pure mesoporous TiO2 and hybrid TiO2–FGSs appears in earlier published papers.16,26 Their characteristic physical properties including crystalline phase, nanostructure, surface area, and pore size are summarized below. For pure mesoporous TiO2, the low-angle X-ray diffraction pattern of mesoporous TiO2 displays a reflection peak at a d-spacing of 7.4 nm, indicative of short-range mesoscale ordering. High angle XRD patterns confirm that as-synthesized materials contain crystalline rutile TiO2 with a small amount of anatase TiO2. Results from nitrogen sorption measurements show type-IV isotherms with a rather narrow size distribution of mesopores. The adsorption data indicate a Brunauer–Emmett–Teller (BET) surface area of 300 m2/g for mesoporous TiO2 after calcination. The average pore size in the calcined mesoporous TiO2 calculated using the Barrett–Joynes–Halenda (BJH) model is 3.1 nm. From our previous studies,16,26 XRD for both pure mesoporous TiO2 and TiO2–FGSs show almost identical patterns (ref 16, Figure 1b and ref 26, Figure 2) containing a majority of rutile TiO2 with the same amount of minor anatase TiO2 of nearly 5% (the detailed quantification of the anatase phase is given in ref 16).

Transmission electron microscopy (TEM) images for both pure mesoporous TiO2 and TiO2–FGSs are displayed in Figure 1. For pure mesoporous TiO2, rodlike rutile nanocrystals are oriented in parallel and interspaced by mesoporous channels (Figure 1a). Aggregates of spherical anatase nanoparticles that reside outside of the nanorod-based mesoporous rutile also are observed. Selected area electron diffraction (SAED) patterns (Figure 1b and c) further confirm the rutile crystalline phase for...
The oriented rodlike nanocrystals and the anatase phase for the spherical nanoparticle aggregates. In agreement with the high angle XRD patterns, a series of high-resolution TEM images shows that the oriented rutile TiO$_2$ nanorods comprise the dominant structures in mesoporous TiO$_2$ in addition to a much lower quantity of spherical anatase nanoparticles. TEM images for hydrid/C$_0$TiO$_2$ graphene are given in Figure 1d and e where the FGSs are covered with rodlike rutile nanocrystals similar to those seen for pure mesoporous TiO$_2$. Both the edge of the graphene sheet and the nanostructure of TiO$_2$ are seen clearly in the high-magnification image of Figure 1d. The nanostructured TiO$_2$ is comprised of parallel rodlike rutile nanocrystals interspaced with the SDS surfactant. This structure is consistent with that observed in our previous studies detailing the formation of mesoporous rutile. On the basis of the high-resolution TEM and XRD data, a schematic drawing for the formation of self-assembled rutile (major phase) and anatase (minor phase) TiO$_2$–FGS hybrid nanostructures is presented in Figure 2 where green rods represent rutile nanocrystals while the planar purple mesh corresponds to an individual graphene sheet.

A comparative study of both pure mesoporous TiO$_2$ and hybrid TiO$_2$–FGSs has been carried out to examine any subtle changes in the porosity and interconnectivity caused by the addition of a small amount of graphene into the networks of mesoporous TiO$_2$ materials. A series of HP $^{129}$Xe NMR spectra were taken under nearly identical conditions for both pure mesoporous TiO$_2$ and hybrid TiO$_2$–FGSs. Figure 3 displays the HP $^{129}$Xe NMR spectra taken at 303 K for pure mesoporous TiO$_2$, self-assembled rutile TiO$_2$–FGS hybrids, and pure bulk functionalized graphene sheets (FGSs), respectively. Each of the three samples was heated to 403 K in a NMR rotor under N$_2$ flow for 10 min and then slowly cooled to 303 K before taking the spectrum shown in Figure 3. Variable-temperature continuous flow HP $^{129}$Xe spectra are given in Figures 4 and 5 for pure mesoporous TiO$_2$ and self-assembled rutile TiO$_2$–FGS hybrids, respectively. The top spectra in Figures 4 and 5 were recorded at 183 K (samples were heat-treated to 403 K for 10 min and then cooled to 173 K for 10 min before taking spectra at 183 K), and the temperature was raised 20 K for each incremental spectrum up to 363 K.

The contrasting spectral features shown in Figure 3 for all three samples are indicative of different pore environments associated with each of these three samples. A sharp resonance peak at 0 ppm is observed in the spectra of all three samples. The 0 ppm peak is associated with the free Xe gas, and the peaks at larger chemical shift correspond to xenon adsorbed within the structure of the material. For pure mesoporous TiO$_2$, we observed two resonance peaks at higher chemical shift. In Figure 3, a broader resonance peak with a larger area is found at 63.7 ppm, whereas a comparatively sharper peak but with a smaller peak area is observed at 73.9 ppm. Similar two resonance peaks were also observed in the variable-temperature spectrum (Figure 4) taken at 303 K for pure mesoporous TiO$_2$. Furthermore, all spectra taken at $T > 283$ K in Figure 4 consistently show two resonance peaks at higher chemical shift for the pure mesoporous TiO$_2$, in agreement with the results from our previous study of pure mesoporous TiO$_2$ using a different instrument. The coexistence of two distinct peaks suggests...
that there are at least two different pore environments in pure mesoporous TiO$_2$ in which Xe can adsorb. Our new HP $^{129}$Xe polarizer provides consistent results when compared to a conventional setup used in the previous study.$^{25}$

In contrast, the HP $^{129}$Xe NMR spectrum in Figure 3 taken for hybrid rutile TiO$_2$–FGSs displays a single relatively narrow peak at 68.7 ppm. A similar peak is also observed in the spectrum taken at 303 K in Figure 5 for hybrid rutile TiO$_2$–FGSs. On the basis of our previous study,$^{25}$ the two resonance peaks for pure mesoporous TiO$_2$ are attributed to pores associated with anatase (at higher chemical shift) and rutile TiO$_2$, respectively. It is interesting to observe substantial spectral changes in HP $^{129}$Xe NMR spectra for mesoporous TiO$_2$ before and after adding a small amount of FGSs. Several factors including pore structure, interconnectivity of the pores, resident surface chemistry, and composition affect the line shape of the $^{129}$Xe NMR resonances. To confirm that functionalized graphene sheets by themselves do not add a new spectral feature to the resonances associated with mesoporous TiO$_2$, we also carried out experiments on these bulk FGSs under the same conditions at 303 K after sample is heated to 403 K for 10 min. The spectrum for pure bulk FGSs in Figure 3 does not show any peaks at higher chemical shifts ($>50$ ppm), suggesting that the FGS by themselves do not add new $^{129}$Xe NMR spectral features to the resonances assigned to the Xe interaction with mesoporous TiO$_2$. Because our XRD and TEM data have shown that both hybrid TiO$_2$–FGSs and pure mesoporous TiO$_2$ are comprised of similar rutile nanorods with the same amount of minor anatase TiO$_2$, the pore structures, the surface chemical structures, and the composition should be similar in both samples. It is surprising then, to observe such significant changes in the line shape of the HP $^{129}$Xe NMR spectrum for hybrid TiO$_2$–FGSs upon adding a very small amount of functionalized graphene.

On the basis of the fact that pure bulk FGSs do not contribute to the HP $^{129}$Xe NMR signal to the resonances associated with the mesoporous TiO$_2$ and that the surface chemistry and composition are identical for pure mesoporous TiO$_2$ and hydride TiO$_2$–FGSs, we conclude that the changes in HP $^{129}$Xe NMR line shapes associated with the mesopores in TiO$_2$ do not result from these factors. In addition, we exclude other factors such as temperature and Xe pressure that could change the $^{129}$Xe NMR spectrum by performing the experiments under the same conditions in terms of temperature and $^{129}$Xe pressure for both samples. Therefore, the interconnectivity of the pores is most likely the main factor that affects the line shape of the $^{129}$Xe NMR resonance for the hybrid TiO$_2$–FGSs. However, it is difficult to imagine that the addition of a small amount of graphene could make such a large change in the interconnectivity of the pores. To induce such changes, the graphene sheets would have to be well separated and spread out uniformly into the network of the mesoporous TiO$_2$. Hence, there is no phase separation between graphene and TiO$_2$ in agreement with the TEM data showing that most TiO$_2$ nanorods are spread out on mostly individual graphene sheets.$^{26}$ FGSs have extremely high surface area (theoretical value of 2630 m$^2$/g) especially when produced as chemically functionalized graphene sheets through the thermal expansion of graphite oxide.$^{29,60}$ It is possible that a small addition of graphene sheet to the rutile TiO$_2$ will impart a significant change to the nanostructure of TiO$_2$. Our Xe NMR data confirm that the graphene sheets are well mixed with the TiO$_2$.

In pure mesoporous TiO$_2$, the anatase particles aggregate near the end of the rutile nanorods (Figure 1).$^{16}$ 2D exchange $^{129}$Xe NMR data have shown that Xe exchanges rapidly between these two environments. The cross peaks in 2D exchange (EXSY) NMR spectra show that exchange takes place between both types of pores and the free gas with a short mixing time of 5 ms, indicating that these two types of pores are well connected. Although the pores are relatively well connected in pure mesoporous TiO$_2$, the observation of two distinct resonances indicates that the exchange rate between the pores in anatase and rutile must be slower than the difference in chemical shift frequencies between anatase and rutile pores. The disappearance of two resonance peaks is most likely due to further increased interconnectivity between the anatase and rutile TiO$_2$ pores for hybrid TiO$_2$–FGSs as compared to those for pure mesoporous TiO$_2$. If the exchange of Xe between anatase and rutile pores is faster than the chemical shift difference between these two types of pores, the $^{129}$Xe NMR spectrum would give one resonance peak averaged over the signals from both pores. As shown in Figure 3, the resonance frequency observed in a coalescence peak for TiO$_2$–FGS is between the two resonance lines observed for pure mesoporous TiO$_2$. Hence, a faster exchange of Xe between pores formed by anatase particles and the mesopore channels comprised of rutile nanorods after insertion of functionalized graphene sheets results in a single resonance peak for the hybrid TiO$_2$–FGSs.

Variable-temperature continuous flow HP $^{129}$Xe spectra for pure mesoporous TiO$_2$ are presented in Figure 4 where the top spectrum was recorded at 183 K; the temperature was raised in 20 K increments to 363 K. Because of the increased adsorption at lower temperature, a larger signal for Xe adsorbed on the pore surfaces was observed as compared to the signal associated with the void space. The slower exchange between the gas phase and adsorbed Xe at reduced temperature results in higher observed chemical shifts. Figure 4 shows two resonance peaks for adsorbed xenon at temperatures from 263 to 363 K. As the temperature decreases, the chemical shifts for both resonances increase, but at different rates. The signals collapse into one peak at temperatures below 263 K. The temperature-dependent $^{129}$Xe NMR data confirm the coexistence of two distinct peaks at temperatures above 243 K, indicating that there are at least two different pore environments in mesoporous TiO$_2$ in which Xe can adsorb.

For comparison, variable-temperature CF HP $^{129}$Xe NMR measurements were also taken for hybrid TiO$_2$ samples in Figure 5. Unlike the two peaks observed for pure mesoporous TiO$_2$ (Figure 3), a single large peak at lower chemical shift is observed for hybrid TiO$_2$–graphene (Figure 4) at temperatures above 283 K. Upon decreasing the temperature, a small peak appears at a lower chemical shift as compared to the main large peak starting at temperatures below 283 K. In contrast to the large peak associated with the pores of rutile TiO$_2$, the chemical shift of this small resonance does not change with the temperature, and the peak becomes broader as the temperature is decreased. This signal is not observable at temperatures below 223 K, which may be because the signal is too broad to be discerned at low temperatures. The temperature behavior for this small peak is rather unusual when compared to those for the peaks that are associated with the pores in nano- or mesoporous silica or high surface area TiO$_2$. On the basis of this unique temperature behavior, the small peak cannot be associated with any pores present in the TiO$_2$ nanostructure alone. We assigned a weak, broad signal around ca. 50–60 ppm at 243–283 K (Figure 5) to xenon interacting with graphene. Because there is no such peak observed in pure mesoporous TiO$_2$ (Figure 4) and both pure mesoporous TiO$_2$ and hybrid TiO$_2$–graphene
The temperature dependence of $^{129}\text{Xe}$ chemical shift upon adsorption to mesoporous TiO$_2$ and hybrid TiO$_2$–graphene hybrid materials is shown in Figure 6 where TiO$_2$ (rutile) and TiO$_2$ (anatase) represent the pores in mesoporous TiO$_2$ that give rise to the $^{129}\text{Xe}$ NMR resonance peaks at lower and higher chemical shifts shown in Figure 3, respectively. Figure 6 shows similar temperature-dependent $^{129}\text{Xe}$ chemical shifts for mesoporous TiO$_2$ (rutile) and TiO$_2$–FGSs, whereas the chemical shift for xenon adsorbed between mesopores of rutile and anatase in mesoporous TiO$_2$ is notably different. It is understandable that we observed similar temperature-dependent chemical shift curves for both hybrid TiO$_2$–graphene and TiO$_2$ (rutile) because the hybrid TiO$_2$–FGSs are comprised principally of rutile TiO$_2$. The contrasting temperature-dependent behavior for TiO$_2$ (rutile) and TiO$_2$ (anatase) can be attributed to the difference in geometric structures between the crystalline anatase and rutile phases.25

Temperature-dependent chemical shift data can be used to determine physical parameters related to the adsorption properties of materials. Variations in the $^{129}\text{Xe}$ chemical shift with temperature can be fit to a parametrized model describing xenon absorption that is based upon a Henry’s law isotherm, as described previously.41 In the fast exchange approximation with weak adsorption, the temperature dependence of the observed chemical shifts, $\delta_{\text{obs}}$, for arbitrary pore sizes can be expressed as:

$$\delta_{\text{obs}} = \delta_{0} \left( 1 + \frac{B}{T e^{-\Delta H_{\text{ads}}/kT}} \right); \quad B = \left( \frac{V_{f}}{S} \right) K_{0}^{-1} \tag{1}$$

where $V_{f}$ is the free volume inside TiO$_2$, $T$ is the temperature, $S$ is a specific surface area, $K_{0}$ is the pre-exponential term of Henry’s constant, $R$ is the universal gas constant, $\Delta H_{\text{ads}}$ is the heat of adsorption, and $\delta_{0}$ is the component of the observed $^{129}\text{Xe}$ chemical shift characteristic of the interaction between xenon and the surface.

Table 1 lists the $\Delta H_{\text{ads}}$ and $\delta_{0}$ values obtained from fits of these variable-temperature chemical shift curves. The $\delta_{0}$ values range from 114 to 122 ppm for mesoporous TiO$_2$ and hybrid TiO$_2$–FGSs samples, which are comparable to the 109 ppm previously reported for nonporous anatase TiO$_2$ obtained using thermally polarized Xe in a sealed high pressure cell.33 It is not surprising to observe similar characteristic chemical shifts because $\delta_{0}$ correlates with the surface chemical composition, and Ti–O chemical bonding predominates in these samples. However, the small variance in $\delta_{0}$ for all samples is due to other subtle differences such as the level of hydration, reduced oxidation state, or the presence of different TiO$_2$ phases. The observed $\Delta H_{\text{ads}}$ values for these samples are in the range from 12 to 16 kJ/mol, which is consistent with what is generally seen for physical adsorption of Xe on solid surfaces; this has been observed before in numerous micro- and mesoporous materials.41,42 Table 1 also shows a larger heat of adsorption of 16.0 kJ/mol for TiO$_2$(rutile) than that of 12.9 kJ/mol for TiO$_2$(anatase). In agreement with the observation of different slopes in temperature-dependent chemical shift data for Xe adsorbed on TiO$_2$(rutile) and TiO$_2$(anatase), the difference in $\Delta H_{\text{ads}}$ values suggests the existence of two types of binding sites for Xe adsorbed on TiO$_2$(rutile) and TiO$_2$(anatase) pore surfaces. Because both rutile and anatase pores are comprised of TiO$_2$, the binding sites are largely determined by the geometries of the pore surfaces. The different geometries of pore surfaces may arise from the coexistence of different crystalline phases such as anatase and rutile TiO$_2$. Hence, TiO$_2$(rutile) and TiO$_2$(anatase) are associated with the anatase and rutile phases, in agreement with the XRD and TEM data.16 Pore diameters for both mesoporous TiO$_2$ and hybrid TiO$_2$–FGSs samples were estimated using empirical chemical shift–pore size correlations developed for inorganic systems like MCMs and zeolites.43,44 Table 1 displays the pore sizes derived from the $^{129}\text{Xe}$ NMR data in the context of both spherical and cylindrical pore models for all TiO$_2$ samples. For a given model, the resonance with a larger chemical shift often corresponds to a smaller pore size. Because the interparticle spacing is representative of more spherical pores than cylindrical pores, it is reasonable to use the spherical pore model to estimate the pore sizes for

![Figure 6. CF HP $^{129}\text{Xe}$ chemical shift for adsorbed xenon as a function of temperature for rutile and anatase pores in mesoporous TiO$_2$ and pores in self-assembled TiO$_2$–FGS hybrids. The dashed lines are a visual guide only.](image-url)
all pores formed from the aggregation of the nanoparticles. However, the cylindrical pore model is best suited for the cylindrical mesoporous channels observed in rutile TiO$_2$ by TEM. Using appropriate models, both rutile and anatase pores in mesoporous TiO$_2$ have similar sizes as shown in Table 1. The results derived in the context of spherical and cylindrical models reported in Table 1 are to be treated as approximations. The pore sizes should be regarded with caution, as there may be an unaccounted scaling factor due to differences in the chemical composition. However, we believe that the result on the comparison of two types of pores is sufficiently reliable. The pore size for rutile TiO$_2$ in hybrid TiO$_2$–FGSs is also similar to that for pure mesoporous TiO$_2$. Even though the chemical shift for TiO$_2$ (anatase) is larger than that for TiO$_2$ (rutile), we obtained similar pore sizes because of the difference in pore geometries. The pore diameter of 3–4 nm for meso-TiO$_2$ determined from the $^{129}$Xe NMR data is in agreement with the TEM and BET results. Unlike BET, $^{129}$Xe NMR allows us to identify pores of similar size in different phases of TiO$_2$.

Our comparative HP $^{129}$Xe NMR results from this study have shown that $^{129}$Xe NMR is a powerful technique for probing any changes in porosity and interconnectivity of the pores caused by the addition of a small amount of functionalized graphene sheet (1 wt %) into the network of mesoporous TiO$_2$. The information on the interconnectivity of the pores is critical for understanding transport properties in porous materials. Such information is difficult to obtain using conventional techniques such as BET, XRD, or TEM. Because spin-polarized Xe gas percolates through the interconnected pores and samples the local pore environments, HP $^{129}$Xe NMR has the unique advantage of directly probing not only these buried interfaces but also the interconnectivity between the pores. On the basis of the comparative HP $^{129}$Xe NMR studies of pure mesoporous TiO$_2$ before and after the insertion of FGSs, the changes in HP $^{129}$Xe NMR spectra upon addition of the functionalized graphene sheets (FGSs) indicate that TiO$_2$ and graphene are mixed uniformly on the nanoscale, and the resulting hybrid nanostructure has higher channel connectivity among different domains. This higher connectivity accompanied by well-separated graphene sheets in the TiO$_2$ nanostructural network may be one of major contributing factors that promotes enhanced lithium insertion/extraction in the hybrid material.

■ CONCLUSIONS

Our $^{129}$Xe NMR study has shown that Xe is sensitive to any change in TiO$_2$ nanostructure upon insertion of a small amount of graphene into the mesoporous network. A relatively narrow $^{129}$Xe single peak is observed for the self-assembled hybrid TiO$_2$–FGSs. In contrast, however, there are two resonance peaks corresponding to rutile TiO$_2$ and anatase TiO$_2$ in pure mesoporous TiO$_2$. The HP $^{129}$Xe NMR results from our comparative study suggest that TiO$_2$ and graphene are mixed uniformly on the nanoscale, and the resulting hybrid nanostructure has better channel connectivity among the resident domains, thereby enhancing Li transport throughout the structure.

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