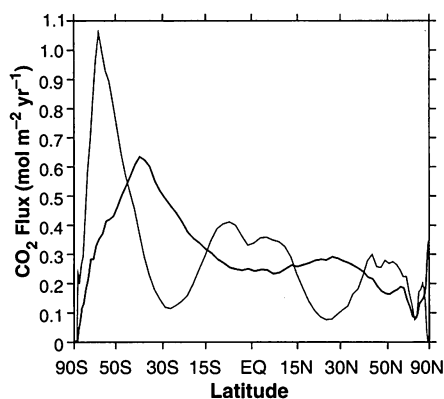




**Fig. 3.** Zonal mean anthropogenic  $\text{CO}_2$  accumulation rate in the ocean (black line) and zonal mean anthropogenic  $\text{CO}_2$  flux into the ocean (magenta line), by latitude band (averaged over land and ocean areas for 1995). The latitude axis is scaled so that equal horizontal distances represent equal areas on Earth's surface. On this scale, the total flux or accumulation into the ocean is proportional to the area under the appropriate curve. The Southern Ocean is an area with the highest anthropogenic  $\text{CO}_2$  fluxes, but the Antarctic Convergence is the area with the largest anthropogenic  $\text{CO}_2$  accumulation.

ern Ocean was much more vigorous in the period from ~1350 to 1880 A.D. than in the recent past. Our simulations reflect primarily late-20th century oceanographic conditions and support the conclusion of a subordinate role for deep convection in the Southern Ocean during this time period (21).

Our conclusion that present-day Southern Ocean uptake of anthropogenic carbon is large, but Southern Ocean storage is relatively small, has implications for the mechanisms governing future changes in the ocean carbon cycle. If most of the anthropogenic carbon entering the Southern Ocean is being transported northward isopycnally to the Antarctic Convergence, then a reduction in deep convection would have little impact on Southern Ocean uptake of anthropogenic carbon. Thus, the particular scenario described in (6) seems unlikely to occur. Changes in ocean circulation, reduction in sea ice coverage, temperature-dependent changes in  $\text{CO}_2$  solubility, and changes in biological activity will impact oceanic  $\text{CO}_2$  uptake (6, 15). Nevertheless, if global climate change reduces the density of surface waters in the Southern Ocean (6, 15), isopycnal surfaces that are now ventilated would become isolated from the atmosphere; this would tend to diminish Southern Ocean carbon uptake.

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## Nanotube Molecular Wires as Chemical Sensors

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Chemical sensors based on individual single-walled carbon nanotubes (SWNTs) are demonstrated. Upon exposure to gaseous molecules such as  $\text{NO}_2$  or  $\text{NH}_3$ , the electrical resistance of a semiconducting SWNT is found to dramatically increase or decrease. This serves as the basis for nanotube molecular sensors. The nanotube sensors exhibit a fast response and a substantially higher sensitivity than that of existing solid-state sensors at room temperature. Sensor reversibility is achieved by slow recovery under ambient conditions or by heating to high temperatures. The interactions between molecular species and SWNTs and the mechanisms of molecular sensing with nanotube molecular wires are investigated.

Carbon nanotubes are molecular-scale wires with high mechanical stiffness and strength. A SWNT can be metallic, semiconducting, or semimetallic, depending on its chirality (1). Utilization of these properties has led to applications of individual nanotubes or ensembles of nanotubes as scanning probes (2, 3), electron field emission sources (4), actuators

(5), and nanoelectronic devices (6). Here, we report the realization of individual semiconducting-SWNT (S-SWNT)-based chemical sensors capable of detecting small concentrations of toxic gas molecules.

Sensing gas molecules is critical to environmental monitoring, control of chemical processes, space missions, and agricultural and medical applications (7). The detection of  $\text{NO}_2$ , for instance, is important to monitoring environmental pollution resulting from combustion or automotive emissions (8). Detection of  $\text{NH}_3$  is needed in industrial, medical, and living environments (9). Existing electrical sensor materials include semicon-

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ducting metal oxides (7–9), silicon devices (10, 11), organic materials (12, 13), and carbon black–polymer composites (14). Semiconducting metal oxides have been widely used for NO<sub>2</sub> and NH<sub>3</sub> detection (7–9). These sensors operate at high temperatures (200° to 600°C) in order to achieve enhanced chemical reactivity between molecules and the sensor materials for substantial sensitivity (7). Conducting polymers (12) and organic phthalocyanine semiconductors (12, 13) have also been investigated for NO<sub>2</sub> or NH<sub>3</sub> sensing. The former exhibit limited sensitivity (12), whereas the latter tend to have very high resistivity (sample resistance of >10 gigohms) (13). In this report, we show that the electrical resistance of individual semiconducting SWNTs change by up to three orders of magnitude within several seconds of exposure to NO<sub>2</sub> or NH<sub>3</sub> molecules at room temperature. Miniaturized chemical sensors based on individual SWNTs are thus demonstrated. Furthermore, we combine theoretical calculations with experiments to address the underlying fundamental question regarding how molecular species interact with nanotubes and affect their electrical properties.

Semiconducting SWNTs are chiral ( $m, n$ ) tubes with  $m - n \neq 3 \times \text{integer}$ . The band gap  $E_g$  of an S-SWNT scales with its diameter  $d$  as  $E_g \propto 1/d$  ( $E_g \propto 0.5$  eV for  $d \sim 1.4$  nm) (1). It

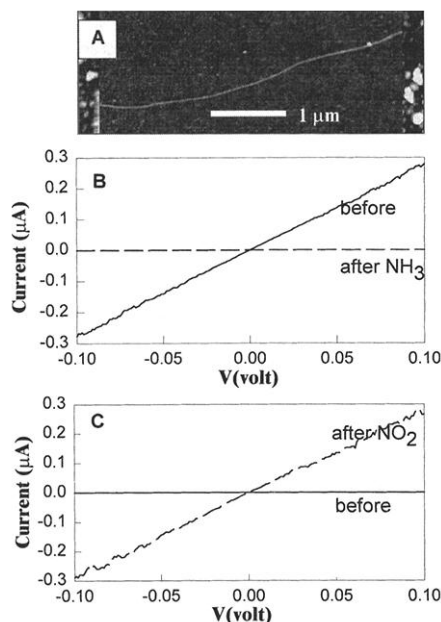
was previously found that when two metal contacts were used to connect an S-SWNT, the metal/S-SWNT/metal system exhibits  $p$ -type transistor characteristics with several orders of magnitude change in conductance under various gate voltages (6, 15, 16). Our nanotube chemical sensors were based on these S-SWNT transistors, obtained by controlled chemical vapor deposition growth of individual SWNTs from patterned catalyst islands on SiO<sub>2</sub>/Si substrates (Fig. 1A) (16, 17). Gas-sensing experiments were carried out by placing an S-SWNT sample in a sealed 500-ml glass flask with electrical feedthrough and flowing diluted NO<sub>2</sub> [2 to 200 parts per million (ppm)] or NH<sub>3</sub> (0.1 to 1%) in Ar or air (flow rate of 700 ml/min) through the flask while monitoring the resistance of the SWNT.

We observed that the conductance of S-SWNT samples can be substantially increased or decreased by exposure to NO<sub>2</sub> or NH<sub>3</sub>. A current versus voltage ( $I$ - $V$ ) curve recorded with an S-SWNT sample after a 10-min exposure to NH<sub>3</sub> showed an  $\sim 100$ -fold conductance depletion (Fig. 1B). Exposure to NO<sub>2</sub> molecules increased the conductance of the SWNT sample by about three orders of magnitude (Fig. 1C) when the SWNT sample was initially depleted by a back-gate voltage ( $V_g$ ) of +4 V (6, 15, 16). The SWNT is a hole-doped semiconductor, as can be gleaned from the current versus gate voltage ( $I$ - $V_g$ ) curve shown in Fig. 2 (middle curve), where the conductance of the SWNT is observed to decrease by three orders of magnitude under positive gate voltages (6, 15, 16). The  $I$ - $V_g$  curve recorded after the S-SWNT sample was exposed to NH<sub>3</sub> exhibits a shift of  $-4$  V (Fig. 2, left curve). In contrast, the  $I$ - $V_g$  curve was shifted by +4 V after NO<sub>2</sub> exposure (Fig. 2, right curve). The low resistance ( $\sim 360$  kilohms) of the SWNT under zero gate voltage suggests substantial hole carriers existing in the  $p$ -type nanotube at room temperature. Exposure to NH<sub>3</sub> effectively shifts the valence band of the nanotube away from the Fermi level, resulting in hole depletion and reduced conductance. For the

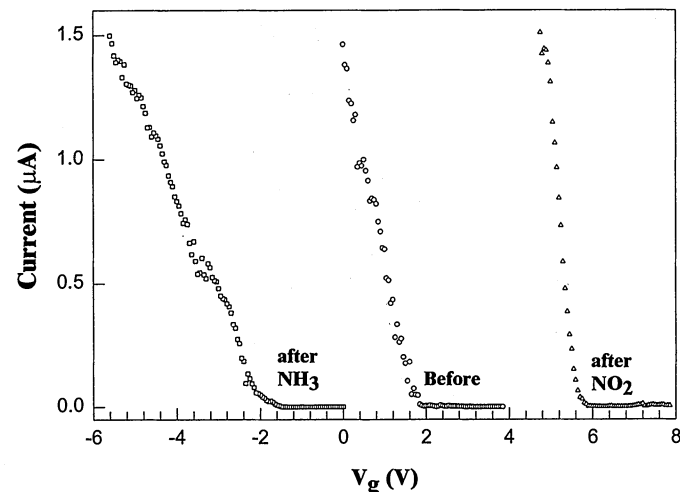
NO<sub>2</sub> case, exposure of the initially depleted sample to NO<sub>2</sub> resulted in the nanotube Fermi level shifting closer to the valence band. This caused enriched hole carriers in the nanotube and enhanced sample conductance. These results show that molecular gating effects are capable of shifting the Fermi level of S-SWNTs and modulating the resistance of the sample by orders of magnitude.

The conductance of the SWNT sample increased sharply by about three orders of magnitude after 200 ppm of NO<sub>2</sub> was introduced (Fig. 3A). We investigated five S-SWNT samples and found that the response times (defined as time duration for resistance change by one order of magnitude) of the samples to 200 ppm of NO<sub>2</sub> were in the range of 2 to 10 s. The sensitivity [defined as the ratio between resistance after ( $R_{\text{after}}$ ) and before ( $R_{\text{before}}$ ) gas exposure] is  $\sim 100$  to 1000. After the NO<sub>2</sub> flow was replaced by pure Ar, the conductance of the SWNT samples was observed to slowly recover, and the typical recovery time was  $\sim 12$  hours. This suggests slow molecular desorption from the nanotube sample and that the SWNT chemical sensors can be reversibly used. Heating the exposed sample in air at 200°C led to recovery in  $\sim 1$  hour. For comparison, a high-performance metal oxide sensor (Cd-doped SnO<sub>2</sub>) operates at 250°C for detecting 100 ppm of NO<sub>2</sub> with a response time of  $\sim 50$  s, a recovery time of  $\sim 8$  min, and a sensitivity of  $\sim 300$  (8, 18). A polypyrrole-conducting polymer sensor can detect 0.1% NO<sub>2</sub> by an  $\sim 10\%$  resistance change in  $\sim 5$  to 10 min at room temperature (12). Thus, the S-SWNT sensors have the advantage of room temperature operation with sensitivity up to  $10^3$  over these materials.

NH<sub>3</sub>-sensing results were obtained with the same SWNT sample after recovery from NO<sub>2</sub> detection (Fig. 3C). The conductance of the SWNT sample was observed to decrease  $\sim 100$ -fold after exposure to a 1% NH<sub>3</sub> flow. The response times to 1% NH<sub>3</sub> for five S-SWNT samples were  $\sim 1$  to 2 min, and the sensitivity was  $\sim 10$  to 100. For comparison,



**Fig. 1.** Changes of electrical characteristics of a semiconducting SWNT in chemical environments. (A) Atomic force microscopy image of a metal/S-SWNT/metal sample used for the experiments. Nanotube diameter is  $\sim 1.8$  nm. The metal electrodes consist of 20-nm-thick Ni, with 60-nm-thick Au on top. (B) Current versus voltage curves recorded before and after exposure to NH<sub>3</sub>. (C) Current versus voltage curves recorded under  $V_g = +4$  V, before and after NO<sub>2</sub> exposure.



**Fig. 2.** Chemical gating effects to the semiconducting SWNT. Current versus gate voltage curves before NO<sub>2</sub> (circles), after NO<sub>2</sub> (triangles), and after NH<sub>3</sub> (squares) exposures. The measurements with NH<sub>3</sub> and NO<sub>2</sub> were carried out successively after sample recovery.

metal oxide  $\text{NH}_3$  sensors typically operate at 300° to 500°C, with a response time of ~1 min and a sensitivity of ~1 to 100 toward 200 ppm to 1%  $\text{NH}_3$  (8). Conducting polymer sensors can detect 1%  $\text{NH}_3$  with a response time of ~5 to 10 min by an ~30% resistance change at room temperature (12).

For the S-SWNT samples, lowering the  $\text{NO}_2$  concentration to 20 and 2 ppm led to response times of ~0.5 to 1 min and ~5 min, respectively (Fig. 3B). Lowering the concentration of  $\text{NH}_3$  to 0.1% led to a response time of ~10 min (Fig. 3D). Thus, for detecting an ~10-fold resistance change of individual S-SWNT samples within minutes of gas exposure, the lower concentration limit is ~2 ppm for  $\text{NO}_2$  and ~0.1% for  $\text{NH}_3$ . Similar sensing results were obtained when Ar or air was used as the carrier gas. This suggests that  $\text{NH}_3$  or  $\text{NO}_2$  dominates the response of the SWNT samples over molecules in the ambient environment. Over time, repeated sensing and recovery experiments with the S-SWNT samples obtained reproducible results.

To understand the chemical gating effects and the nanotube gas-sensing mechanism, we first considered the fact that S-SWNT samples appear to be hole doped (*p*-type) before the molecular sensing experiments. Hole doping in S-SWNTs has been observed by several groups (6, 15, 16). Possible hole-doping mechanisms include metal electrode-tube work function mismatch (6) and electrostatic effects due to charged species existing on the  $\text{SiO}_2$  surface or bulk (19). Because our nanotubes are long (>3

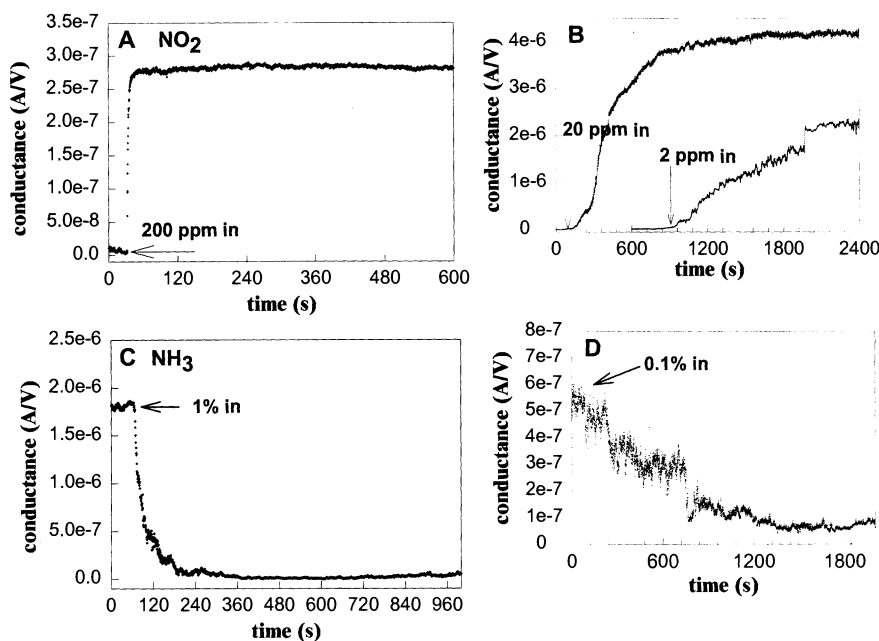
$\mu\text{m}$ ), we suggested a hole-doping mechanism (for example, charged chemical groups on  $\text{SiO}_2$ ) operating throughout the nanotube length. As a result of the hole doping, the Fermi level of an S-SWNT is typically located at ~25 meV above the valence band (19), which is responsible for the observed conductance of S-SWNT samples at room temperature (typical resistance of 300 kilohms to 5 megohms). Next, we considered the chemical nature of the molecules.  $\text{NO}_2$  has an unpaired electron and is known as a strong oxidizer. Upon  $\text{NO}_2$  adsorption, charge transfer is likely to occur from an SWNT to  $\text{NO}_2$  because of the electron-withdrawing power of the  $\text{NO}_2$  molecules.  $\text{NH}_3$ , on the other hand, is a Lewis base with a lone electron pair that can be donated to other species. However, it is necessary to investigate whether these qualitative pictures represent the correct mechanisms of molecular sensing with SWNTs.

We carried out first-principles calculations on molecule-SWNT complexes using density functional theory (20).  $\text{NO}_2$  is found to bind with a semiconducting (10, 0) tube with an adsorption energy  $E_a \sim 0.9$  eV (18.6 kcal/mol) and 0.1 electron charge transfer from the tube to a  $\text{NO}_2$  molecule. Charge transfer from the nanotube to  $\text{NO}_2$  should be the mechanism for increased hole carriers in an S-SWNT and enhanced conductance. For the  $\text{NH}_3$ -SWNT system, calculations found no binding affinity between  $\text{NH}_3$  molecules and the (10, 0) tube. We suggest two possible indirect routes through which  $\text{NH}_3$  molecules may affect S-SWNTs. The first is that  $\text{NH}_3$

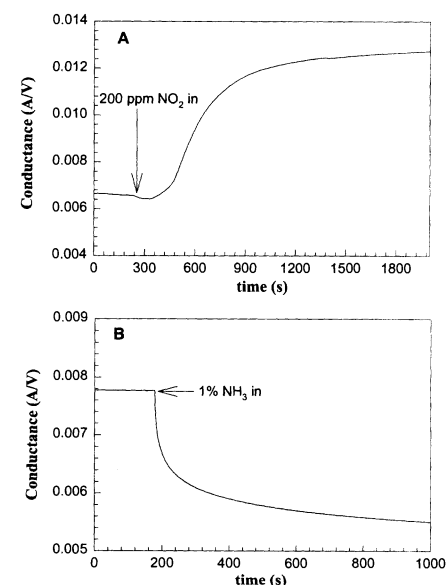
binds to hydroxyl groups on the  $\text{SiO}_2$  substrate (21), which could partially neutralize the negatively charged groups on the  $\text{SiO}_2$  surface and lead to positive electrostatic gating to the S-SWNT. Second, interactions may exist between  $\text{NH}_3$  molecules and an SWNT through other species. It was previously found that  $\text{NH}_3$  can interact strongly with adsorbed oxygen species on graphite (22). Preadsorbed oxygen species on a nanotube could interact with  $\text{NH}_3$  and affect its electrical properties. These possible mechanisms require further experimental and theoretical investigations.

We also investigated the electrical properties of metallic SWNTs in various chemical environments. A metallic tube was identified by small changes in the conductance with gate voltage (a typical resistance of ~20 to 200 kilohms) (16). We found that, for a typical metallic SWNT, exposure to  $\text{NO}_2$  or  $\text{NH}_3$  increased or decreased, respectively, the conductance of the sample by  $\leq 30\%$ . The explanation for these small changes is that, for a metallic SWNT, small shifts of the Fermi level do not result in a substantial change in the density of states at the Fermi level and, thus, in the charge carriers in the nanotube.

The interactions between  $\text{NO}_2$  and  $\text{NH}_3$  with graphite have been previously investigated (22–25). For SWNTs, molecular interaction effects have been studied in the case of Br and I intercalation with bulk samples of SWNT ropes (26, 27). The intercalation leads to substantially enhanced sample conductance (26, 27). Our report is concerned with molecular interactions with individual semiconducting and metallic



**Fig. 3.** Electrical response of a semiconducting SWNT to gas molecules. (A) Conductance (under  $V_g = +4$  V, in an initial insulating state) versus time in a 200-ppm  $\text{NO}_2$  flow. (B) Data for a different S-SWNT sample in 20- and 2-ppm  $\text{NO}_2$  flows. The two curves are shifted along the time axis for clarity. (C) Conductance ( $V_g = 0$ , in an initial conducting state) versus time recorded with the same S-SWNT sample as in (A) in a flow of Ar containing 1%  $\text{NH}_3$ . (D) Data recorded with a different S-SWNT sample in a 0.1%  $\text{NH}_3$  flow. Read  $3.5\text{e-}7$ , for example, as  $3.5 \times 10^{-7}$ .



**Fig. 4.** Electrical response of bulk SWNT mats to  $\text{NO}_2$  and  $\text{NH}_3$  molecules. (A) Conductance versus time data recorded with an SWNT mat in 200 ppm of  $\text{NO}_2$ . (B) Conductance versus time recorded with an SWNT mat in 1%  $\text{NH}_3$ .

SWNTs. We have also investigated the effects of NO<sub>2</sub> and NH<sub>3</sub> on the electrical properties of mats of SWNT ropes made from as-grown laser ablation materials. In a 200-ppm NO<sub>2</sub> flow, the resistance of an SWNT mat is found to decrease from  $R = 150$  to  $80$  ohms ( $R_{\text{before}}/R_{\text{after}} \sim 2$ ) in  $\sim 10$  min (Fig. 4A). In a 1% NH<sub>3</sub> flow, the resistance of a second SWNT mat increases from  $120$  to  $170$  ohms ( $R_{\text{after}}/R_{\text{before}} \sim 1.5$ ) in  $\sim 10$  min (Fig. 4B). In these bulk SWNT samples, the molecular interaction effects are averaged over metallic and semiconducting tubes. Also, the inner tubes in SWNT ropes are blocked from interacting with NO<sub>2</sub> and NH<sub>3</sub> because the molecules are not expected to intercalate into SWNT ropes. This explains the small resistance change of bulk SWNT mats by gas exposure compared to that of an individual S-SWNT.

The main feature of individual S-SWNT sensors, besides their small sizes, is that they operate at room temperature with sensitivity as high as  $10^3$ . An individual nanotube sensor can be used to detect different types of molecules. The selectivity is achieved by adjusting the electrical gate to set the S-SWNT sample in an initial conducting or insulating state. The fast response of a nanotube sensor can be attributed to the full exposure of the nanotube surface area to chemical environments. Thus, nanotube molecular wires should be promising for advanced miniaturized chemical sensors.

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## Single-File Diffusion of Colloids in One-Dimensional Channels

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Single-file diffusion, prevalent in many processes, refers to the restricted motion of interacting particles in narrow micropores with the mutual passage excluded. A single-filing system was developed by confining colloidal spheres in one-dimensional circular channels of micrometer scale. Optical video microscopy study shows evidence that the particle self-diffusion is non-Fickian for long periods of time. In particular, the distribution of particle displacement is a Gaussian function.

Single-file diffusion (SFD) occurs when the individual pores of the medium are so narrow that the particles are unable to pass each other (1, 2). The sequence of particles remains unchanged over time, and thus, the basic principle of diffusion as a physical mixing process comes into question. The concept of SFD was originally introduced more than 40 years ago in biophysics to account for the transport of water and ions through molecular-sized channels in membranes (3); since then, in addition to biological systems (4, 5), SFD is also discussed in the context of interaction of Markov chains in statistics (6), the transportation of adsorbate molecules through zeolites (2), and charge-carrier migration in one-dimensional (1D) polymer and superionic conductors (7). Furthermore, SFD is also related to surface growth phenomena through some mapping (8).

As the mutual passage of particles is prohibited in single-filing (SF) systems, the movements of individual particles are correlated, even at long time periods, because the displacement of a given particle over a long distance necessitates the motion of many other particles in the same direction. This correlation is reflected in the long-time behavior of the mean-square displacement (MSD), which has been predicted for an infinite system to be (6, 7, 9–11)

$$\langle \Delta x^2 \rangle = 2F\sqrt{t} \quad (1)$$

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where  $F$  is the SF mobility and  $t$  is time. Accordingly, SFD processes, in contrast to 2D and 3D self-diffusion seen in colloidal systems (12), cannot be described by a diffusion coefficient; that is, the SFD does not obey Fick's laws.

Experimental evidence confirming non-Fickian behavior was unavailable for a long time because of the lack of ideal experimentally accessible SF systems. Recently, measurements of SFD became feasible in artificial crystalline zeolites. Adsorbate molecules, like methane or CF<sub>4</sub> with diameters of 3.8 and 4.7 Å, respectively, confined in AlPO<sub>4</sub>-5 zeolite with a pore size of 7.3 Å, are considered to be good realizations of SF systems. Although some experimental evidence for the occurrence of SFD was found by pulsed field gradient nuclear magnetic resonance study (13, 14), some results from different groups and experimental methods are still in contradiction, even for the same system (15, 16), as indicated by Hahn and Kärger (17), who suggest and explore several possible reasons. Other effects, such as attractive particle interaction (18), the possible existence of correlations between particles of neighboring pores (19), have also been shown to play a vital role in the mechanism and rates of intracrystalline diffusion. Because of the shortage of structural information on the atomic level, the mechanism of molecular diffusion in zeolites, however, is still under debate.

We created a well-defined SFD model system by confining paramagnetic colloidal spheres of several micrometers in a set of circular trenches fabricated by photolithography. The channels are well-characterized, and the particle-particle interaction can be precisely adjusted by an external magnetic field. Moreover, because the time and length scales in such a colloidal system are easily accessed