Effect of 16-mercaptohexadecanoic acid modification on liquid transport in a nanoporous carbon

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The inner surfaces of a nanoporous carbon are modified by 16-mercaptohexadecanioic acid. The degree of wettability is electrically controllable: by applying a negative potential difference across the solid-liquid interface, the ion transport pressure in the nanopores can be considerably lowered; while the effect of applying a positive potential difference is negligible. These phenomena can be attributed to the unique surface chain configuration in the confining nanoenvironment. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3149826]

Modifying surface properties has long been an active research area, which is of both prime scientific interest and important technological relevance.[1] It provides a variety of mechanisms for controlling contact behaviors of liquids and solids, leading to the development of advanced techniques of liquid conduction, surface reaction, adhesion, etc.[2,3] Usually, a flat solid surface is used as the substrate, on which surface groups are strongly bonded. If the surface group density is sufficiently high, the access to the substrate is blocked and the surface properties are dominated by the grafted layers.

Recently, treating inner surfaces of nanoporous materials has draw increasing attention.[4,5] With the nanopore walls being covered, their properties can be tailored in wide ranges for catalysis, drug delivery, absorption and adsorption, separation and purification, and energy-related applications.[6,7] Many treatments are focused on adjusting the surface wettability. For instance, it has been shown that as the inner nanopore surfaces are appropriately treated, due to the thermocapillary or electrocapillary effect, the degree of hydrophobicity of the material can vary upon environmental changes.[8,9] Consequently, with the aid of an external pressure field a liquid phase can infiltrate into or defiltrate from the nanopores.[10–12] Such systems have great potential for smart catalysis and controlled separation/purification.

Usually, the properties of a treated surface are permanent; that is, unless degradation or leaching occurs, its behavior cannot be changed. To produce a "switchable" surface, the length of the surface groups must be sufficiently long and the chain configuration should be field responsive, so that the surface morphology can be adjusted. This concept has been investigated for large solid surfaces.[13,14] The surfaces groups can be long chains with charged end groups. As a potential difference is applied normal to the solid-liquid interface, the chain may be either bent or straight, exposing different chain sections to the exterior, and thus the overall surface properties are controllable. In the current study, we investigate a nanoporous carbon to answer the following question: whether the inner surfaces of nanopores can also be electrically adjustable.

The nanoporous carbon material was provided by Cabot (BP2000). By using a Micromeritics ASAP-2000 porosimetry analyzer, its specific nanopore volume was measured as 2.2 cm^3/g, the specific nanopore area was 1200 m^2/g, and the average nanopore size was 17 nm. The material was in powder form. The particle size was about 50 μm. The material surface was cleaned in a tube furnace at 450 °C in nitrogen for 12 h, followed by repeated washing in acetone and warm water and vacuum drying at 80 °C for 12 h. The surface treatment agent was chosen as 16-mercaptohexadecanoic acid (MHA).[15,16] Its molecular formula is HS(CH$_2$)$_{15}$CO$_2$H. The body of the chain is formed by trans-CH$_2$ links, which are hydrophobic.[17] The carboxylate end group is negatively charged, which may respond to an external electric field. The MHA was injected into dry toluene in a round-bottom flask with the mass ratio of 15 mg per ml. The mixture was stirred gently for 20 min at room temperature when 480 mg of nanoporous carbon was added. By using a thermal mantle, the temperature was maintained at 95 °C and the carbon-liquid mixture was refluxed for 72 h. Then, the carbon powders were filtered and thoroughly rinsed by dry toluene, acetone, and warm water, and dried in vacuum at 120 °C for 12 h. The surface reaction happened at the hydroxyl sites.[5,18]

The treated BP2000 was uniformly mixed with polyvinylidene fluoride, with the mass ratio of 4:1. The mixture was compressed in a steel mode by a type 5580 Instron machine under 5 MPa, forming disk-shaped electrode. The diameter of the electrode disk was 12 mm and the thickness was 0.5 mm. In a stainless steel cylinder, as depicted in Fig. 1, the electrode was separated from a platinum counterelectrode by a 50 μm thick porous polyethylene membrane separator and immersed in 20% aqueous solution of lithium chloride (LiCl). The electrolyte was added to enhance the liquid conductivity. The system was sealed by a steel piston. The inner surface and the bottom of the cylinder were insulated by thin Teflon layers. By using a DC power supply, a potential difference could be applied across the electrode and the counterelectrode. The voltage was 0, +0.5, or −0.5V.

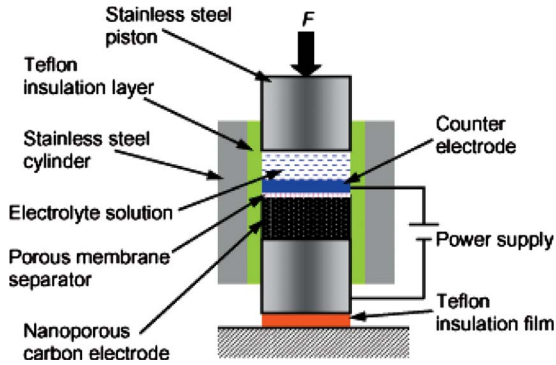a)Author to whom correspondence should be addressed. Electronic mail: yqiao@ucsd.edu.

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FIG. 1. (Color online) Schematic of the experimental setup.

FIG. 3. (Color online) Schematic of the surface groups at (a) an uncharged surface; (b) a negatively charged surface; and (c) a positively charged surface.

Redox reactions might happen if the magnitude of the interface potential difference was further increased. As the voltage was maintained constant, the upper piston was compressed into the cylinder by a type 5580 Instron machine, applying a quasihydrostatic pressure on the liquid phase. The piston speed was 0.5 mm/min. When the pressure reached about 14 MPa, the piston was moved out at the same speed. Typical sorption isotherm curves are shown in Fig. 2. The specific volume change was defined as the ratio of the decrease in system volume to the mass of the BP2000 in the electrode.

During the refluxing process, the MHA chains are grafted at the graphene surface. If the surface chains were straight, the negatively charged carboxylate end groups would attract polar water molecules, so that the surface is hydrophilic. Under this condition, when the electrode is immersed in an aqueous solution, the nanopores would be soaked up spontaneously. As an external pressure is applied by the piston, the system response should be quite linear, with the pressure-volume slope dominated by the liquid bulk modulus. However, Fig. 2 shows clearly that under ambient pressure the nanopores are empty. When a hydrostatic pressure is applied, it builds up a potential in the bulk liquid phase outside the nanoporous particles: $U=P^2V/2B$, where P is the pressure, V is the liquid volume, and B is the bulk modulus, which is around 2 GPa for aqueous solutions.[19] Thus, the driving force for liquid infiltration is $dU/dV=P^2/2B$. At the equilibrium condition, the driving force is balanced by the effective infiltration resistance $R=\Delta\gamma\cdot A$,

where $\Delta\gamma$ is the excess solid-liquid infiltration tension and A is the increase in solid-liquid interface area. For the sake of simplicity, assume that $A\approx2V/r$, with r being the effective nanopore radius. Hence, $dR/dV=2\cdot\Delta\gamma/r$. For a given r, $U=R$ and $dU/dV=dR/dV$ must be satisfied at the same pressure, at which with an infinitismal increment in P, $U>R$, and $dU/dV>dR/dV$. Not only it is energetically favorable for the liquid phase to enter into the nanopores (V tends to decrease) but also the driving force of infiltration increases; that is, the bulk liquid phase becomes unstable. It continuously transforms to the confined liquid phase inside nanopores, until the nanopores are filled. The critical pressure is $P_{in}=2\sqrt{B\cdot\Delta\gamma}/r$. Because the pore size of the BP2000 distributes in a certain range, the infiltration begins with the relatively large nanopores and end with the relatively small ones, resulting in the infiltration plateau in sorption isotherm curve. The width of the plateau is around 2 cm^3/g, similar to the measured porosity, as it should be. The profile of the infiltration plateau is determined by the pore size distribution.

Since the nanopore surfaces are hydrophobic, the grafted MHA groups must be in the bent configuration, as depicted by Fig. 3(a). As the carboxylate end groups are buried by the chain bodies, the hydrophobic CH$_2$ groups are exposed to the liquid phase, and thus the nanopores are effectively nonwettable. This is confirmed by the testing result that, once a negative 0.5 V voltage is applied across the solid-liquid interface, the infiltration pressure considerably decreases; i.e., the degree of hydrophobicity, $\Delta\gamma$, is reduced. As shown in Fig. 3(b), at a negatively charged surface, the carboxylate end groups are repelled and the MHA chains tend to be straight. Hence, the polarity of the effective solid-liquid interface increases. Note that even at −0.5 V, the nanopore surfaces are still hydrophobic, suggesting that only a relatively small portion of the MHA chains are straight. This may be attributed to the confinement effect of the nanopore walls that were frequently reported in recent research.[20,21] Since the opposite walls are relatively close to each other, the negatively charged end groups repel each other against the graphene surface, so that the MHA chains tend to be bent. When the external electric field is applied, the surface electrostatics effect is suppressed and thus more chains are straight.

If the applied voltage is positive, as shown in Fig. 2, the variation in sorption isotherm curve is negligible, since such a potential difference would not cause much change in configuration of bent surface groups [Fig. 3(c)]. According to Fig. 2, upon the application of the negative voltage, the most pronounced variation in P_{in} happens at the beginning of the infiltration plateau, where P_{in} is relatively low and the corresponding pore size is relatively large. At the end of the plateau, where the nanopore size is relatively small, the varia-
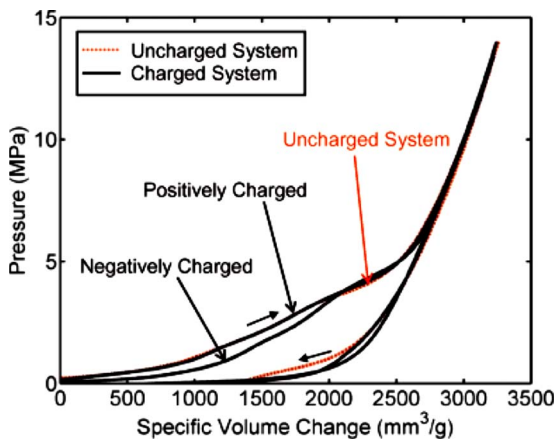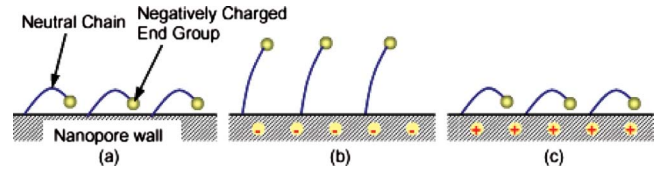
FIG. 2. (Color online) Typical sorption isotherm curves. Each curve consists of a loading part and an unloading part, respectively, reflecting the system volume decrease/increase as the external pressure increases/decreases.

tion in sorption isotherm curve is secondary. Clearly, the effect of MHA groups is reduced in the smallest nanopores, probably because of the difficulty in infiltration of the relatively large MHA molecules in the surface treatment process.

To summarize, it is validated experimentally that the wettability of inner surfaces of nanopores can be electrically controllable, with the modification of morphing surface groups. The confinement effects of nanopore walls lead to the unique surface configuration and the pore size dependence of modification effect.

[1] A. W. Adamson and A. P. Gast, *Physical Chemistry of Surfaces* (Wiley, New York, 1997).
[2] J. P. Matinlinna and P. K. Vallittu, J. Contemp. Dent. Pract. **8**, 1 (2007).
[3] G. L. Witucki, J. Coat. Technol. **65**, 57 (1993).
[4] M. H. Lim and A. Stein, Chem. Mater. **11**, 3285 (1999).
[5] A. Han and Y. Qiao, Chem. Lett. **36**, 882 (2007).
[6] A. Han, X. Chen, and Y. Qiao, Langmuir **24**, 7044 (2008).
[7] A. Han and Y. Qiao, Langmuir **23**, 11396 (2007).
[8] X. Kong and Y. Qiao, J. Appl. Phys. **99**, 064313 (2006).
[9] A. Han and Y. Qiao, Appl. Phys. Lett. **91**, 173123 (2007).
[10] A. Han and Y. Qiao, J. Mater. Res. **22**, 644 (2007).
[11] A. Han and Y. Qiao, Philos. Mag. Lett. **87**, 25 (2007).
[12] Y. Qiao, V. K. Punyamurtula, A. Han, X. Kong, and F. B. Surani, Appl. Phys. Lett. **89**, 251905 (2006).
[13] C. S. Tang, M. Dusseiller, and S. Makohliso, Anal. Chem. **78**, 711 (2006).
[14] G. Chen, G. T. McCandless, and R. L. McCarley, Lab Chip **7**, 1424 (2007).
[15] J. Lahann, S. Mitragotri, T. Tran, H. Kaido, J. Sundaram, I. S. Choi, S. Hoffer, G. A. Somorjai, and R. Langer, Science **299**, 371 (2003).
[16] Y. Liu, L. Mu, B. Liu, S. Zhang, P. Yang, and J. Kong, Chem. Commun. (Cambridge) **2004**, 1039.
[17] Y. Xia and G. M. Whitesides, Angew. Chem., Int. Ed. **37**, 550 (1998).
[18] A. Han, W. Lu, V. K. Punyamurtula, T. Kim, and Y. Qiao, J. Appl. Phys. **105**, 024309 (2009).
[19] D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (Oxford University Press, Oxford, 2005).
[20] X. Gong, J. Li, H. Lu, R. Wan, J. Li, J. Hu, and H. Fang, Nat. Nanotechnol. **2**, 709 (2007).
[21] J. Li, X. Gong, H. Lu, D. Li, H. Fang, and R. Zhou, Proc. Natl. Acad. Sci. U.S.A. **104**, 5824 (2007).