

Electrically controlled hydrophobicity in a surface modified nanoporous carbon

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Conventional surface treatments lead to constant surface morphologies and properties. Here we show that as the inner surfaces of a nanoporous carbon are modified by 16-mercaptohexadecanoic acid through a two-step grafting process, due to the flexibility of the surface chains, the end groups can be repelled by negative surface charges and attracted by positive surface charges. Thus, the surface wettability is controlled electrically. The effective solid-liquid interfacial tension in the nanopores is analyzed in a pressure induced infiltration experiment. © 2011 American Institute of Physics. [doi:10.1063/1.3549295]

At the nanometer scale, surface phenomena become dominant, primarily due to the ultralarge surface to volume ratio.¹ Surface processes that are negligible at macroscopic level can be greatly amplified, which is one of the key reasons why nanomaterials became an active area of research in the past couple of decades. For instance, the excess solid-liquid interfacial tension, $\Delta\gamma = \gamma_{sl} - (\gamma_s + \gamma_l)$, is typically at the level of a few 10^2 mJ/m²,² much smaller than the surface free energy of a solid material, with γ_{sl} being the solid-liquid interfacial tension and γ_s and γ_l the surface tensions of solid and liquid, respectively. However, if liquid-solid contact and separation can be achieved in a nanoporous material, because the specific surface area (A) is 10^2 – 10^3 m²/g,³ the associated energy change can be 10–100 J/g,⁴ causing a considerable temperature variation.⁵

Very often, the surface properties of a nanomaterial need to be modified to meet the functional requirements. A powerful method is to perform surface grafting treatment. With a coating layer, the surface properties can be entirely changed. The commonly used surface groups include silyl materials, which can react with the hydroxyl sites at a solid surface and form relatively strong bonds.⁶ Before the treatment, the hydroxyl sites make the surface quite polar and, thus, hydrophilic.^{7,8} After the treatment, the silyl groups are non-polar and the surface tends to be hydrophobic. Similar concept can be extended to other surface reactions, so that the surface properties can be adjusted in broader spectra.⁹

Conventional surface treatment techniques lead to fixed surface morphologies. Once the surface groups are grafted, their configurations would not change, except that in a harsh environment they may degrade. For instance, if the temperature is higher than a critical level surface chains can decompose and the surface treatment effects are reduced.¹⁰ As an external thermal or electric field is applied, the effective surface tension can vary due to the well known thermowetting and/or electrowetting phenomena.^{11–13} However, these changes are relatively weak. In a changing working environ-

ment, it is often desirable that the surface properties can be adjusted in broad ranges, e.g., for smart catalysis, controlled drug delivery, nanotransportation/microtransportation, etc. For these applications, the surface groups should be field responsive and adjustable. One method is to use surface chains of charged end groups. The chains should be relatively long and flexible, and their configurations are influenced by surface charges.¹⁴ Previously, studies on controllable surface chains were focused on outer surfaces of particles and fibers,¹⁵ compared with which controlling inner surfaces of nanoporous materials was relatively uninvestigated. The difficulty comes from the lack of understanding and control of diffusion, absorption and desorption, grafting, and temperature and electric field effects in the confining nanoenvironment.

In the current study, a nanoporous carbon (Cabot BP2000) was employed as the model material. The material was in fine powder form, with the particle size around 50 μm . Its nanoporous structure was characterized by a Micromeritics TriStar-3000 analyzer, and the results are shown by the upper-left inset in Fig. 1. The material was heated at 450 °C in nitrogen for 12 h, followed by furnace cooling. It was washed in acetone and warm water repeatedly for three times, and then vacuum dried at 80 °C for 10 h. The surface

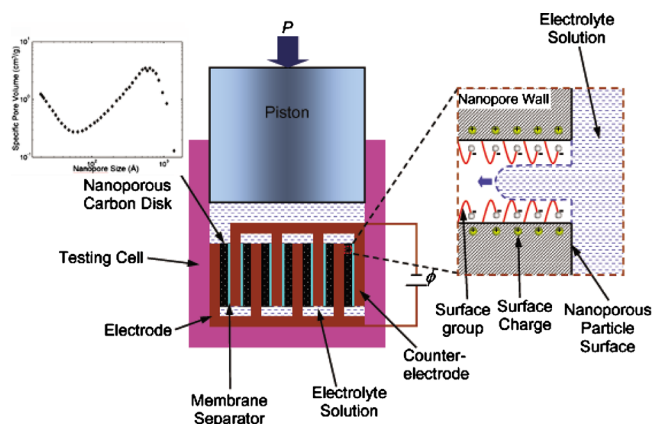


FIG. 1. (Color online) Schematic of the experimental setup.

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treatment consisted of two steps. The first step followed the silyl treatment procedure investigated by Lim and Stein.¹⁶ After drying, 870 mg of BP2000 powders were immediately sealed in a round-bottom flask with 40 ml of dry toluene containing 1.0 ml of chlorotrimethylsilane. The mixture was first stirred at 10 rpm at room temperature for 10 min, and then at 100 rpm at 90 °C for 2 h. The treated material was rinsed by dry toluene, acetone, and warm water, and dried in vacuum at 120 °C for 12 h. After the first step, a monolayer of silyl groups were grafted at nanopore surfaces. The surface density of silyl groups was relatively high while there were still hydroxyl sites available for further surface treatment.¹⁷

In the second step, the surface was treated by 16-mercaptohexadecanoic acid (MHA), $\text{HS}(\text{CH}_2)_{15}\text{CO}_2\text{H}$. A MHA chain has 15 trans carbon-carbon bonds, which is relatively flexible and nonpolar (hydrophobic). Once it reacted with the hydroxyl sites at the carbon surface, the other end was capped by a negatively charged carboxylate (CO_2H) group, which was hydrophilic. The grafting was performed in the round-bottom flask. In 40 ml of dry toluene containing 2.0 ml of MHA, the BP2000 sample was refluxed at 95 °C for 36 h. The treated material was filtered, washed in acetone and distilled water repeatedly, and dried in air.

The surface treated BP2000 powders were mixed uniformly with acetelyene black (AB) and polyvinylidene fluoride (PVF), with the mass ratio of 8:1:1. The AB and PVF particles were solid and, therefore, did not affect the porosity. The mixture was compressed at 8 MPa into thin disks, with the diameter of 12.7 mm and the thickness of about 0.2 mm. The carbon disk was conductive, with the resistivity of about $20 \mu\Omega \text{ m}$. A multilayer electrode was produced by repeatedly folding a gold foil. The carbon disks were inserted in between the gold layers, as depicted in Fig. 1. Between two adjacent gold layers, two carbon disks were separated by another gold layer. The extra gold layers were connected together, forming the counterelectrode. The carbon disks and the counterelectrode were insulated by porous Teflon membranes. The membrane thickness was 50 μm . The system was immersed in a 15% aqueous solution of lithium chloride (LiCl) and sealed in a steel cylinder. The electrode was insulated from the testing cell by a Teflon tape. A constant voltage, ϕ , was applied by a dc power supply between the electrode and the counterelectrode. The applied voltage was 0.48, 0, or -0.48 V .

The degree of hydrophobicity of the nanopore surfaces was measured by intruding the LiCl solution into the nanopores. The pressure was applied by a type 5580 Instron machine through a piston, at a constant rate of 0.5 mm/min. As the pressure was increased to 14 MPa, the piston was moved out at the rate of -0.5 mm/min . Typical sorption isotherm curves at different voltages are compared in Fig. 2.

According to the gas absorption analysis, the nanopore size distribution is bimodal. The lower peak is at 1–2 nm, and the higher peak is at about 54 nm. The specific nanopore surface area is nearly $1200 \text{ m}^2/\text{g}$. The porosity is around 70%. In the first step of the surface treatment, the nanopore walls are covered by hydrophobic silyl groups; in the second step, the grafted surface groups are MHA chains. As depicted in the inset in Fig. 1, if the MHA chains are bent, the hydrophobic chains are exposed to the liquid phase. If the MHA chains are straight, the charged carboxylate end groups

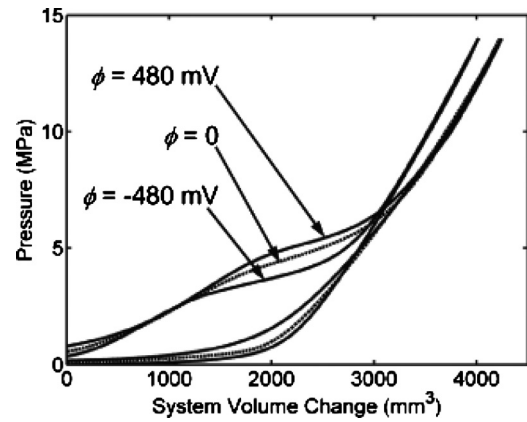


FIG. 2. Typical sorption isotherm curves.

would attract water molecules and oppositely charged ions. The dashed line in Fig. 2 shows that the overall effect of the two types of surface groups makes the nanopore walls effectively hydrophobic. Thus, when the applied pressure P is relatively low, the liquid phase cannot enter the nanopores. When $P \approx 3.5 \text{ MPa}$, the repelling effect of the nanopore wall is overcome. Associated with the liquid infiltration, the system volume decreases rapidly as the pressure is increased. According to the classic Laplace–Young equation, the infiltration pressure P_{in} can be related to the interfacial tension $\Delta\gamma$ as $P_{\text{in}} = 4\Delta\gamma/D$, where D is the effective nanopore size. Hence, the infiltration pressure of the small nanopores (1–2 nm) should be higher than that of the large nanopores (50–60 nm) by more than an order of magnitude, and the sorption isotherm curve may contain two distinct infiltration plateaus. Such two-staged structure, however, is not observed in the current pressure range, suggesting that the smallest nanopores are not involved in the infiltration process. The slope of the infiltration plateau reflects the variation in nanopore size, as shown in Fig. 3. The value of excess interfacial tension, $\Delta\gamma$, is set as 33.5 mJ/m^2 , such that the nanopore size at 50% infiltration volume fits with the higher peak of the gas absorption analysis result (54 nm). This value is comparable with but higher than the effective interfacial tension of silyl treated surfaces,¹⁸ suggesting that the MHA groups increase the degree of hydrophobicity.

Once a voltage is applied, positive surface charges tend to attract the negatively charged carboxylate groups of MHA chains; and, thus, they are fully bent. Under this condition, the hydrophilic components are “shielded” by the hydropho-

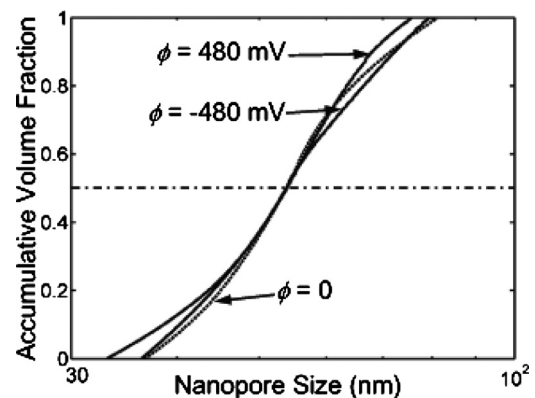


FIG. 3. The calculated accumulative nanopore volume distribution curves.

bic components. The testing data in Fig. 2 indicate that the infiltration pressure increases considerably. Through a similar analysis of the pore size distribution, the effective interfacial tension can be determined as 36.7 mJ/m^2 , higher than that of uncharged system by nearly 10%. The increase in infiltration pressure is quite uniform in the entire infiltration plateau, indicating that the surface charge effects are independent of the nanopore size. It also implies that, without the external electric field, the MHA chains are only partly straight; otherwise the attraction electric force would not cause detectable variation in surface property.

When the direction of the applied voltage is reversed, the surface charges become negative, which tend to repel the like-charged carboxylate groups. Hence, the MHA chains become straight, and the hydrophilic components are exposed to the confined liquid, leading to the decrease in effective interfacial tension. From the nanopore size distribution analysis (Fig. 3), it is calculated that the effective value of $\Delta\gamma$ is lowered to 26.5 mJ/m^2 , about 20% smaller than that of the uncharged system. Clearly, the carboxylate groups can no longer be shielded. The negative charge effect is more pronounced than the positive charge effect, which may be attributed to the initial partly bent configuration of the MHA groups. Similar to the positively charged system, the variation in infiltration pressure is uniform.

To summarize, through a two-stepped treatment procedure, the inner surfaces of a nanoporous carbon can be modified by MHA. Initially, the surface groups are partly bent, and the nanopore walls are hydrophobic. The surface prop-

erties can be controlled by an electric field, as the negatively charged carboxylate groups are repelled or attracted by the surface charges.

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