Superhydrophobic Carbon Films

Superhydrophobicity of Nanostructured Carbon Films in a Wide Range of pH Values**

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Superhydrophobic surfaces whose water contact angle (CA) is larger than 150° has aroused great interest.[1–4] Over the past 60 years there have been numerous reports concerning the

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study of such surfaces.[5–17] It is concluded that a superhydrophobic surface can be effectively fabricated by combining appropriate surface roughness with materials of low surface energy, and the presence of a compound that contains fluorine is often necessary. Among the reported studies, we have also made some progress. For example, we reported that nanostructured aligned carbon nanotube films with a fluoroalkysilane coating show "superamphiphobic" properties, that is, CAs for both water and oil are larger than 150°.[18] Based on this study, we recently demonstrated the preparation of polymer nanofibers, whose surfaces have superhydrophobic properties with CAs larger than 170° even without any modification, by using materials of low surface energy.[19] A coating consisting of nanofibers exhibits a surface structure that is believed to cause superhydrophobicity. This effect can be observed in nature on the leaves of the lotus.[20] The as-prepared superhydrophobic surfaces have great potential in not only fundamental research but also practical applications. For example, they can be effectively used for textiles, traffic signs, hulls of ships, tubes or pipes, building glass, windshields of cars, satellite antenna, and conductors with a self-cleaning surface.[5,21] However, such surfaces are not available in different pH environments. Although polytetrafluoroethylene (PTFE) films are chemically resistant, they are only reported to be superhydrophobic for pure water.[22] Until now, no superhydrophobic surfaces suitable for all pH environments have been prepared.

Herein we report the formation of nanostructured carbon films through a facile and typical pyrolysis pathway.[23] Nanosturctured polyacrylonitrile (PAN) films prepared according to reported procedures[19a] were used as the precursor. Interestingly, the as-prepared films show superhydrophobic property in the pH range from 1.07 to 13.76. That is, water CAs are larger than 150° for not only pure water but also corrosive liquids, such as acidic and basic solutions. It is believed that the formation of nanostructured graphitelike structures causes this unique property. From the point of practical applications, this kind of surface will be more useful in the fabrication of chemical engineering materials and microfluidic devices.[24–26]

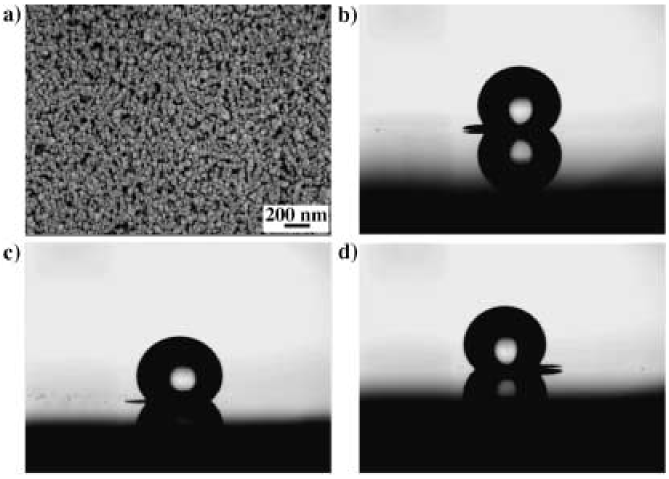

Figure 1. a) SEM image of the top view of the as-prepared nanostructured carbon films; pictures showing the water contact angles of the nanostructured carbon films; the pH values are: b) pH 7.08, c) pH 1.07, and d) pH 13.76.

Figure 1 a shows the scanning electron microscopic (SEM) image of the top view of the as-prepared nanostructured carbon films. The average diameter of the carbon fibers and the interfiber distance are about 39 ± 3 nm and 50 ± 4 nm, respectively. Carbon nanofibers that consist of films are perpendicular to the substrate of the anodic aluminum oxide membrane, and the thickness of the films can be controlled in the range from 7 to 15 μm. These nanostructured films are rough enough and are regarded as a composite consisting of fibers and air, the latter is present in the troughs between individual carbon nanofibers. As such a rough structure can induce superhydrophobicity,[4–21] these films are expected to have special wettability properties. Figure 1 b shows the shape of water droplet (about 1.5 mm in diameter, pH 7.08) on the carbon films, the CA here is about 161.2 ± 2.7°, namely, the obtained films are superhydrophobic. Figure 1 c and 1 d show the shapes of aqueous solution droplets with pH values of 1.07 and 13.76, respectively, on the nanostructured carbon films. Surprisingly, these two droplets remain spherical with CAs larger than 150° (158.9 ± 2.3° and 159.3 ± 1.7°, respectively). High CAs for both the acidic and basic droplets on any kind of solid surfaces have never been reported before. It is very important that the superhydrophobic carbon films can be used in all pH environments for corrosive liquids.

To determine the effect of pH values on CAs for the nanostructured carbon films, further studies were developed in detail. Figure 2 shows the relationship between pH values and CAs on the nanostructured carbon films. There is no obvious fluctuation of the CA value within the errors. All CA values are in the range from about 154.1° to 164.2°, with little difference coming from experimental error. This result indicates that pH values of the aqueous solution have little or no effect on CAs for as-synthesized carbon films. It confirms that the nanostructured carbon films are superhydrophobic in the pH range from 1.07 to 13.76.

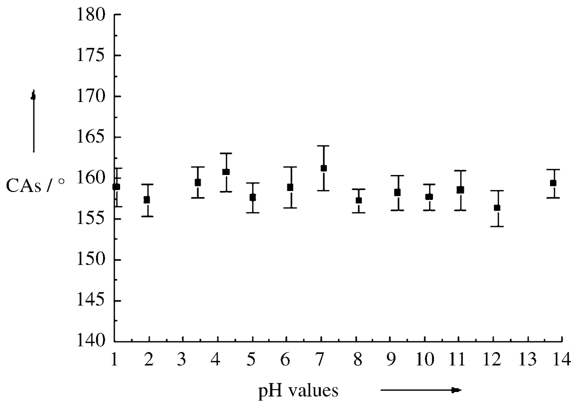

Figure 2. Graph showing the relationship between pH values and contact angles on the nanostructured carbon films.

The formation process of carbon films can be characterized by Fourier transform infrared (FTIR) spectroscopy (Figure 3).[27] The pyrolysis temperature employed in our

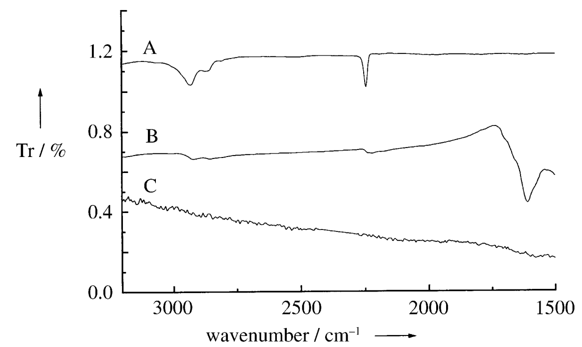

Figure 3. FTIR spectra of the representative samples: A) PAN nanofiber films, B) Cyclized PAN nanofiber films after treatment at 220 °C for 1 h in air, C) Carbon films after carbonization at 900 °C for 1 h under a nitrogen atmosphere. Tr = transmittance

study was 900 °C, which is far below the graphite formation temperature ranging from 1500–2000 °C. Therefore, the carbon materials formed here are in a graphitelike state. X-ray photoelectron spectroscopy (XPS) spectra (Figure 4) show a main asymmetric peak centered at 284.6 eV with a long tail extended to the higher energy region, which is characteristic graphite.[28] This peak can originate from both sp^2-hybridized graphitelike carbon atoms and from carbon atoms bonded to hydrogen atoms, and has been explained in terms of many electron interactions of the metallic conduction electrons, induced by low energy electron-hole excitations, which result from the absorption of the X-rays. The other broad peak, shown in Figure 4, which corresponds to a higher binding energy at 287.8 eV, is considered to originate from carbon atoms bonded to one, two, and three oxygen atoms because the electronegative oxygen atoms induce a positive charge on a carbon atom. According to the calculated result from the real XPS spectra, the relative intensity of the peak representing graphite is greater than 91 %, which is close to the ideal for purified multiwall carbon nanotubes with a graphitelike structure.[29] Therefore, we conclude that the as-synthesized carbon films have graphitelike structure.

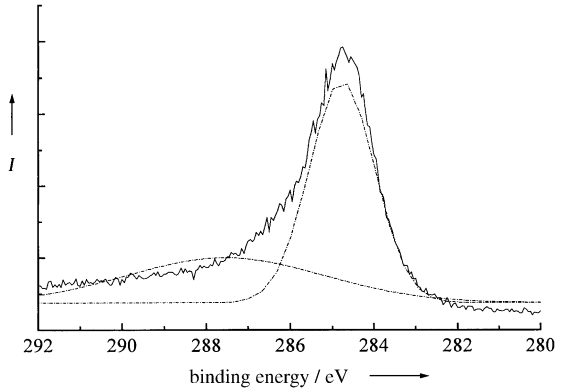

Figure 4. X-ray photoelectron spectra illustrating the C$_{1s}$-core of nanostructured carbon films. *I* = intensity (arbitrary units); —— real XPS spectra; –•–• fit to a Gauss–Lorenz function.

Graphitelike carbon has intrinsic properties of thermal and chemical resistance, which can be used in strongly acidic or basic liquids. The results of wettability measurement indicate that CAs on the surface of a fresh graphite plane are all in the range of 80–85° for pure water, acidic and basic solutions (see Supporting Information). Nanostructured graphitelike carbon films were reported to be stable in an acidic or basic solution at normal temperature, and oxidized only when subjected to strong oxidation treatment, such as reflux at 140 °C in a mixture of concentrated nitric and sulphuric acid (1:3 in volume ratio).[30] In our study, no changes, including both structure and hydrophobicity, are found when the nanostructured carbon films are dipped into strong alkali and acid for 24 h (See Supporting Information). The contact angles of these films remain larger than 150° after dipping them in alkaline and acidic solutions (within the instrument and measurement error). In contrast, the precursor of PAN nanofiber films is easily eroded, and the nanostructures are destroyed.

In conclusion, nanostructured graphitelike carbon films were prepared through a simple pyrolysis method. The as-prepared films are superhydrophobic for not only pure water but also corrosive liquids, such as acidic and basic solutions. This is the first example of superhydrophobicity over the whole range of pH values without the presence of fluorine-containing compounds, and might open up new perspectives in preparing novel nanoscale interfacial materials.

Experimental Section

The formation processes of nanostructured carbon films included cyclization and carbonization: PAN nanofiber films were first cyclized at 220 °C for 1 h in air, followed by further carbonization at 900 °C for 1 h under a nitrogen atmosphere.[23] PAN nanofibers films prepared according to reference [19a] were used as the precursor to obtaining carbon films.

SEM image was obtained with a JEOL JSM-6700 scanning electron microscopic at 3 kV. CAs were measured on a dataphysics OCA20 contact-angle system at ambient temperature. Water droplets (about 5 μL) with different pH values were dropped carefully onto the nanostructured carbon films. The average CA value was obtained by measuring at five different positions of the same sample. FTIR spectra were performed on a Bruker EQUINOX55 Fourier transform infrared spectrometer. XPS spectra were recorded by using a VG ESCALAB MKII spectrometer with an Al$_{K\alpha}$ monochromatic X-ray source.

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[27] Two stretching vibration bands from CH_2 stretching ($\sim 2931\,cm^{-1}$) and C≡N ($\sim 2243\,cm^{-1}$) are observed in sample A. Both bands are strong, revealing the presence of PAN. The corresponding absorptions are weak in the spectrum of sample B, and a new band appear at $\sim 1594\,cm^{-1}$ originating from the C=N bond after cyclization. In the spectrum of sample C, all characteristic bands disappear, thus indicating the carbonization from the cyclized structure.

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