A new approach to fabricate superhydrophobic and antibacterial low density isotropic pyrocarbon by using catalyst free chemical vapor deposition

Tan, Ruixuan; Xie, Hongyan; She, Jueqin; Liang, Jingshi; He, Hao; Li, Jianghua; Fan, Zheqiong; Liu, Bo

2019

Tan, R., Xie, H., She, J., Liang, J., He, H., Li, J., . . . Liu, B. (2019). A new approach to fabricate superhydrophobic and antibacterial low density isotropic pyrocarbon by using catalyst free chemical vapor deposition. *Carbon*, 145, 359-366. doi:10.1016/j.carbon.2019.01.041

<https://hdl.handle.net/10356/144547>

<https://doi.org/10.1016/j.carbon.2019.01.041>

©2019 Elsevier Ltd. All rights reserved. This paper was published in *Carbon* and is made available with permission of Elsevier Ltd.

Downloaded on 26 Apr 2023 13:59:25 SGT

A new approach to fabricate superhydrophobic and antibacterial low density isotropic pyrocarbon by using catalyst free chemical vapor deposition

Ruixuan Tan^b, Hongyan Xie^c, Jueqin She^a, Jingshi Liang^a, Hao He^a, Jianghua Li^d, Zheqiong Fan^{a*}, Bo Liu^{a*}

^a College of Materials Science and Engineering, Changsha University of Science and Technology, Changsha 410114, China.

^b State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China

^c China-Australia Institute for Advanced Materials and Manufacturing, Jiaying University, Jiaying 314000, China

^d School of Chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, Singapore 637459, Singapore

Abstract

Low density isotropic pyrocarbon (LDIP) of a novel “litchi” hierarchical structure with a high degree of crystallinity and graphitization was prepared by a simple, catalyst-free chemical vapor deposition method. The fabricated LDIP coating surface exhibits highly durable and robust superhydrophobic, self-cleaning, water and corrosive liquids repelling and oil-water separating properties. Moreover, the antifouling/antibacterial properties and biocompatibility of LDIP were investigated. The LDIP coated surface can not only effectively prevent protein and bacterial (Gram-negative *E. coli*) adhesion but also has good biocompatibility. This new type of carbon material has great promise for potential applications in waste water treatment and biomedical fields.

*Corresponding author. E-mail: fzq1987@126.com, lbb1107@126.com

1. Introduction

Isotropic pyrocarbon (ISO Pyc), a subclass of the carbon depositions on substrate formed by thermal pyrolysis of gaseous hydrocarbons in an activated environment, has been widely applied in biology, aerospace and nuclear industries, such as making artificial heart valves and mechanical sealing devices in aero-engine, and also the components of composite coating for holding the fission radioelements of fuel particles [1-3]. To fulfill the requirements of these applications, excellent biological compatibility, super impermeability and especially good mechanical properties which are largely in relation with its density are needed [4]. Generally, low density ISO Pyc (LDIP), indicative of lack of sufficient strength advantage, may consider to be of little value for these applications. Hence, the fabrication of high density ISO Pyc has been the main goal in majority of corresponding researches [5-7]. However, it is found that a special kind of LDIP has a striking characteristic of inherently stable superhydrophobicity, while the high density ISO Pyc doesn't possess.

Superhydrophobic surfaces are characterized normally with a static contact angle (CA) higher than 150° [8]. Thanks to the fascinating water repelling ability, superhydrophobic surfaces have attracted widespread scientists' interest in solid/liquid interface associated fields, such as anticorrosion, anti-icing, drag reduction and oil-water separation [9-11]. Appropriate surface roughness and low surface free energy are of the two essential elements of superhydrophobicity [10]. So far, the effort in superhydrophobic surfaces building has been focused on two aspects: one is to introduce roughness onto low-surface-energy materials, that is, natural hydrophobic materials. Many complicated methods such as plasma treatment [12], template methods [13] or etching methods [14] have been developed to construct micro- and nanohierarchical structure. The other is to modify the rough surfaces by using low-surface-energy materials, for example inorganic/organic oxides [15,16] or fluorides [17,18], but they might not be resistant to harsh conditions, such as high temperature and strong acid/base, as well have certain biological toxicity so that may inevitably affect the actual use[19,20].

In consideration of practical applications, selecting an economical, non-toxic material to prepare superhydrophobic surfaces has been attracting much more attention. Among the numerous reported low-surface-energy materials, carbon materials are becoming a strong candidate for fabricating superhydrophobic surfaces in recent years, due to their high electricity [21], remarkable light-absorption [22], excellent high temperature and chemical resistance [23]. For example, Jiang et al. [24] utilized template method to develop superhydrophobic surface of aligned carbon nanofibers. Liu et al. [25] prepared robust lotus-like carbon nanotube film with superhydrophobicity via chemical vapor deposition with the assistance of Fe catalyst. Zeng et al. [26] fabricated a vacuum-assembling superhydrophobic multilayer of carboxylated and aminated multiwalled carbon nanotubes with further modification of n-octadecylamine. These developed carbon nano-materials have demonstrated their superiority in superhydrophobic field. Another important usage of carbon materials is for antibacterial and antifouling fields. For example, graphene is regarded as a highly effective antibacterial and antifouling material, since sharp graphene edges can quickly destroy their membranes [27]. As well, carbon nanotubes can provide a strong invitation to polar water molecules while reject salts and pollutants due to low energy consumption, and have antifouling and self-cleaning functions [28]. A major issue is, however, that less biocompatibility caused by the remaining metal ions, the catalysts when these carbon materials grow. Hence, developing a facile, reliable and effective method to prepare superhydrophobic, antifouling and biocompatible carbon material is still in demand.

In this work, we developed a facile, one-step chemical vapor deposition (CVD) method without the assistance of catalyst to directly fabricate a novel type of superhydrophobic carbon material—LDIP based on the previously achieved high density ISO Pyc technology [29]. The LDIP is composed of nanoparticles with specific morphology and microstructure which create a micro/nanoscale “litchi” hierarchical structure and generate inherent superhydrophobic and superoleophilic properties for surfaces without any modification. The as-made superhydrophobic surfaces were suitable for all pH environments and exhibited outstanding durability

and robustness, and showed a good separation efficiency and reusability when used for oil-water separation. Furthermore, the experiments of protein adsorption, bacterial adhesion and cell viability demonstrated the remarkable antifouling/antibacterial and biocompatibility functions of the superhydrophobic surfaces. This simple yet effective and environment-friendly technique provides a promising way of large-scale production of superhydrophobic materials for waste water treatment and biomedical fields.

2 Experimental

2.1 Materials

Methyl blue, Sudan I, sodium chloride (NaCl), polyvinylidene fluoride (PVDF) and N-methyl-2-pyrrolidone (NMP) were all purchased from Beijing Chemical. 3-[4, 5-dimethylthiazoyl-2-yl]-2, 5-diphenyl tetrazolium bromide (MTT), dimethyl sulfoxide (DMSO), and phosphate buffer saline (PBS) were bought from Alfa Aesar. Lysogeny Broth (LB) agar and bicinchoninic acid (BCA) protein kit were supplied by Thermo Fisher, USA.

2.2 Fabrication of LDIP materials

The CVD furnace used in this paper is homemade. As shown in Figures 1a and 1b, the apparatus is composed of three parts: gas intake system, reactor and exhaust gas treatment system. In gas intake system, propylene was used as carbon source, hydrogen and argon were used as carrier and diluted gases. Moreover, hydrogen gas here played the role of controlling the whole pyrolysis reaction process [29]. These three gases were uniformly mixed with flow rates $V_{\text{Propylene}}:V_{\text{Hydrogen}}:V_{\text{Argon}} = 1:15:10$, the same as those reported in the previous paper [29], before introduced into the reactor. But here a revised design of high temperature zone of reactor was utilized for obtaining a suitable residence time of reactive gases, as can be seen in Figure 1b, so that LDIP can be deposited on the graphite disk substrate ($\Phi 110 \text{ mm} \times \Phi 28 \text{ mm}$) at the same temperature of 1550 °C and ambient pressure. The photograph of a part of original LDIP deposit after 30 h deposition is displayed in Figure 1c.

Figure 1 (a) schematic diagram of the CVD apparatus; (b) sectional view of the high temperature zone of CVD reactor; (c) light photograph of a part of original LDIP deposit.

2.3 Characterization

For convenience all the LDIP samples were characterized as powder through finely powdered the original bulk deposits in an agate mortar. The morphology and microstructure of samples were analyzed by scanning electron microscopy (SEM, Hitachi SU8010), Raman spectroscopy (Jobin Yvon LabRAM Aramis spectrometer, $\lambda_0=532$ nm) and transmission electron microscopy (TEM, FEI TF 20). The roughness of surfaces made of LDIP powders were characterized by Atom Force Microscope (AFM, Bruker edge AFM) and 3D Optical Microscope (Bruker Contour GT-K).

Surface wettability was measured using a Biolin Attention Theta to determine the wettability of the surface. The static water contact angle (WCA) testing process was done under ambient conditions by the sessile drop method. A droplet of deionized water was pumped out onto samples. Images of WCA were then captured and calculated by the built-in microscope and software respectively. The volume of the tested water droplet is 10 μ L. The sliding angles (SAs) of the drops were measured by tilting the sample plate from zero to a higher angle until the droplet rolled off the surface.

In oil-water separation experiments, a superhydrophobic oil-water separation membrane using filter paper as the substrate was fabricated briefly as follows: the membrane slurry was prepared by mixing LDIP powder and PVDF at a weight ratio of 9:1 dispersed in NMP. The slurry was then coated on filter paper and dried at 40 °C in a vacuum for 12 h. Dichloromethane and hexane were selected as the representatives of oil with different densities, respectively. A mixture containing 100 ml dichloromethane and 125 ml deionized water dyed with methyl blue, or a mixture containing 60 ml hexane and 40 ml deionized water dyed with methyl blue were prepared. And in experiment of oil adsorption, the membrane was also utilized as absorbent, and dichloromethane colored with Sudan I was chosen as adsorbate and mixed with water. Self-cleaning effects of the LDIP surfaces were studied by contaminating the surfaces using NaCl particles, and then removing the contaminants using water droplets.

The protein adsorption on the surface was determined using BCA assay [30]. The standard calibration curves of bovine serum albumin (BSA), were prepared following the recommended protocol from the manufacturer first. Aluminum foil and LDIP coated aluminum foil (radius = 0.5 cm) were rinsed in PBS buffer (pH = 7.4) for 12h, and then immersed in pure BSA solutions (5 mg/mL in PBS) at 37 °C for 24 h. After this, the coatings were washed using PBS and deionized water thrice, respectively. The coatings were then put into a clean 12-well plate and added with 500 µL of 2.0 wt% sodium dodecyl sulfate (SDS) aqueous solution in each well, subjected to shaking for 1h, and sonicated for 1h at room temperature to remove the absorbed protein from the films. 100 µL of each protein washing solutions were transferred to a new clean 96-well plate, and then another 100 µL of the BCA assay reagent was added, mixed for 3 min on a plate shaker. After incubation at 60 °C for 1h, the absorbance of the protein concentration in the washing solution was measured at 560 nm with Nanodrop 2000 spectrophotometer (Thermo scientific, USA). The antibacterial ability of the coatings against *E. coli* was evaluated. First, culturing the bacterial suspension for 24h and appropriately diluted to concentration of 1×10^6 CFU/mL, the samples that consist of sterilized aluminum foil and LDIP coated aluminum foil were immersed

into bacterial suspension and cultured at 37 °C for 24h. The samples were removed, washed with sterilized PBS solution, put into 1 mL sterilized PBS solution and sonicated for 5-6 min. Then obtained bacterial PBS suspensions were diluted, then 100 μ L diluted suspensions was spread on Lysogeny Broth Agar (LB Agar) plates incubating at 37 °C for 24h, colony forming units' number could be observed and calculated.

In vitro biocompatibility was investigated using 3T3 cell line. Briefly, 3T3 cells were cultured in Dulbecco's Modified Eagle's Medium (DMEM) supplemented with 10% fetal bovine serum (FBS) and 1% antibiotics (penicillin/streptomycin) in 37 °C CO₂ incubator. Cells were harvested when 80% confluence was reached, and cells concentration was counted and calculated with a haemocytomete. 1×10^4 cells/well were seeded into a 96-well plate and grown for 24 hours; followed by 24 hours treatment with varied concentration of polymers, cell viability was then qualitatively evaluated with microscopy and quantified via MTT assay following manufacture's protocol. The cell viability was expressed as a ratio of cell population size treated with polymer compared to control (cells without polymer treatment). To determine IC₅₀ (concentration which reduces cell population by 50% with respect to control), each polymer was tested using the above protocol with 8 concentrations ranging from 8 μ g/mL to 512 μ g/mL and the resulting viability data was linearly regressed to find the IC₅₀ value.

3. Results and discussion

In an earlier study, we proposed a novel fixed-bed CVD method to prepare large sized high density bulk ISO Pyc materials with an apparent density of 1.85 g/cm³, which possessed excellent mechanical and physical properties [29]. Meanwhile some LDIP with an apparent density of 0.90 g/cm³, grown on the graphite substrate, would inevitably be formed at the early deposition stage (Figure S1). As one of imperfections existing in depositions, LDIP was harmful to the product of interest, that is, uniformly-microstructured high density ISO Pyc, which can be removed by surface grinding. To our delight, we found that these “harmful” by-products

unexpectedly had good performance of water repellency with water droplet easily rolling off in a short time, indicating good hydrophobicity (Video S1). In this respect, this kind of carbon materials is expected to be new hydrophobic materials, comparing with carbon black, carbon nanotubes, PAN based carbon fibers and amorphous carbon nanobeads[21-25].

Figure 2 (a) Light photograph of the water droplets on LDIP coated surface; (b) WCA of LDIP coated surface; (c) water SA of LDIP coated surface; (d) oil CA of LDIP coated surface.

To investigate the surface wetting performance of the as-prepared LDIP coating, the WCA and water adhesion property were characterized comprehensively. As can be seen in Figure 2a, different volumes of water droplets are standing on the surface as a nearly perfect spherical shape, indicating good water repellence of the LDIP. The results of wettability measurement imply that the WCA and SA can reach up to 160° and 2.8°, respectively, suggesting that the as-prepared LDIP presented stable superhydrophobicity and very low water adhesion (Figures 2b and 2c). In addition, it is believed that the LDIP surfaces are also superoleophilic according to Figure 2d in which the oil CA of surface is 0°.

Figure 3 (a) SEM (low magnification x 600) of LDIP; (b) SEM (high magnification x 35,000) of LDIP; (c) bright field TEM of LDIP; (c) dark field TEM of LDIP (the inset is a magnified HRTEM image of a nanoparticle); (e) low-loss EELS of LDIP; (f) Raman spectrum of LDIP.

It is generally accepted that the micro/nanoscale surface structure is the critical factor affecting the wettability of the carbon materials [31]. Hence, the morphology and microstructure of LDIP were analyzed firstly. A typical SEM image of as-made LDIP surface is given in Figure 3a. It can be seen that the material has a homogeneous and porous morphology and mainly consists of agglomerates made of fine globular carbon particles. High magnification SEM observation of these globular particles shows that they are not isolated but entangled together with a diameter ranging from 500 nm to 600 nm (Figure 3b), which can provide the material the micro-island and nano-protruded morphology. It should be noted that there are numerous multifaceted nanocrystallites with a similar pyramidal structure on these nanoparticles (marked by arrows in Figure 3b), which looks like the “litchi” structure. Such “litchi” surface structure is a typical hierarchical micro/nanostructure, playing the key role of

superhydrophobicity. Figure 3c and 3d are TEM images of the nanoparticles. As the bright field TEM image (Figure 3c) show, the polygonal boundaries of these nanoparticles can be clearly observed, this is consistent with the SEM results. And the divergent diffraction contrasts in the nanoparticles indicate various orientation of carbon layer stacks. From the dark field TEM image (Figure 3d), a symmetrical cone can be obviously observed in these nanoparticles, implying a relatively high degree of crystallinity with carbon layers preferentially oriented with an interlayer spacing approaching that of graphite (the inset image of Figure 3d). However, it must be pointed out that on a micrometer scale, these particles are isotropic because of their spherical appearance and inner symmetrical conical structure. Moreover, the graphitization degree of these nanoparticles was also analyzed by using Electron Energy Loss Spectroscopy (EELS). Figure 3e shows the low-loss EELS collected from these nanoparticles, giving a $\pi+\sigma$ plasma energy of 26.8 eV that is very close to that of graphite crystal (about 27.0 eV), thus verifying the high graphitic character of the nanoparticles. In addition, analysis of structural information on micrometer scale of the samples was conducted by using Raman spectroscopy. The result is shown in Figure 3f. Two bands, one at around 1350cm^{-1} (D band) and the other 1580cm^{-1} (G band) are visible, respectively. The D band is characteristic of disordered graphite, whereas the G band is corresponding to an undisturbed graphitic lattice. Generally, the intensity ratio of D band and G band (I_D/I_G) is used to evaluate the degree of ordering within the carbon materials. A higher value means a lower degree of ordering, thus a lower level of graphitization. And in our case, a relatively low I_D/I_G ratio of 0.17 suggested a high level of graphitization of the nanoparticles, in good agreement with other analysis results.

In order to further investigate the micro-nano structure of LDIP surfaces, 3D Optical Microscope and AFM were utilized to characterize the roughness of surfaces on different scales. The three-dimensional image and two-dimensional and roughness profile on millimeter and micrometer scales are given in Figure 4 and Figure S2, respectively. It can be found that the LDIP surfaces showed a hierarchical and rough morphology with the extremely high root mean square roughness (R_q) of $1.682\text{ }\mu\text{m}$,

which was in line with the SEM analysis. It could be inferred therefore that the inherent superhydrophobicity of LDIP is attribute to the micro-nano hierarchical structure and intrinsically low surface energy of carbon materials with high graphitization degree. And the large WCA and the low SA of the LDIP surfaces mean a typical Cassie state[32,33]. The dual-scaled air bubbles are trapped between the nanoparticles and within multifaceted nanocrystallites on each single particle, and thus endowed the LDIP surface a nano-Cassie state to repel water droplets.

Figure 4 (a) 3D surface structure; (b) corresponding 2D image; (c) 2D roughness profile of the surface made of LDIP powder characterized by 3D Optical Microscope.

The LDIP, therefore, can be expected to be a new type of oil/water separation materials, since it has good superhydrophobicity and superoleophilicity of water and oil, respectively. The separation membrane was prepared by mixing 90 wt% LDIP powder and 10 wt% PVDF. The influence of the PVDF adhesive on the superhydrophobic property of membrane was investigated, the results of which were summarized in Figure S3. Although PVDF is hydrophobic, the increasing amount of PVDF would have a negative effect on the superhydrophobicity of the membrane. Here, dichloromethane and hexane were used to demonstrate the applicability of membrane for oils with different densities. When the mixture of dichloromethane and

methyl blue dyed water were poured onto the as prepared membrane, the mixture was separated into two layers immediately. Colorless organic phase quickly infiltrated and permeated the LDIP coated membrane and dropped into the Erlenmeyer flask below, whilst the blue water phase was remained on the membrane due to the superhydrophobic nature of LDIP (Figure 5 and Video S2). After separation process, dyed water did not appear in the Erlenmeyer flask, indicating that the superhydrophobic/superoleophilic LDIP coated membrane had separated oil and water completely. The separation process of hexane-water mixture is given in Video S3. With the separation apparatus, the oil-water separation efficiency was calculated by the weight ratio of oil collected in Erlenmeyer flask and the original oil content, the value of which is 97.21% and 96.23% for dichloromethane-water and hexane-water mixtures, respectively. And the influence of separation cycles on separation efficiency was also studied. As the separation cycles increased to 20, the separation efficiency remained stable higher than 90% for two mixtures (Figure S4), indicating remarkable recyclability and reusability.

Figure 5 Separation process of oil-water mixture (dichloromethane and methyl blue dyed water).

Figure 6 6(a)–6(d) show the self-cleaning process of contamination of NaCl crystals on superhydrophobic LDIP surface; 6(e)–6(g) show the capture process of dichloromethane dyed with Sudan I by using the superhydrophobic membrane.

In general, the superhydrophobic surface in Cassie state is endowed with self-cleaning ability, arising from its high water repellency and low water adhesive force. The self-cleaning property of the LDIP coating was demonstrated with NaCl crystals as the contaminant. Some NaCl crystals were dispersed on the LDIP coated surface. A water droplet contacted and then moved on the LDIP coated surface. The NaCl crystals were completely collected by the water droplet, which was not captured with the surface, demonstrating the self-cleaning ability of LDIP coated surface (Figures 6a-6d, Video S4 and Video S5). Furthermore, the LDIP coated surface has

not only the oil/water separation and self-cleaning properties, but also selective oil/water adsorption property, as evident from the Figures 6e-6g and Video S6. The membrane which used in the oil-water separation experiments was immersed in the bottom of water to contact the dichloromethane drops dyed with Sudan I. The membrane can easily absorb the dichloromethane in a few seconds, with left the transparent water layer.

The stability and durability of superhydrophobic surfaces are very important parameters for practical applications. To investigate the stability of the superhydrophobic property of the LDIP coated surface, the effects of both the exposure time to the air and the water solution with different pH values ranging from 1 to 14 were studied. After exposure to air at room temperature for 24 weeks, the coating still had the WCAs as high as 160° without any remarkable decrease comparing to the initial state (Figure 7a), demonstrating excellent air stable of superhydrophobicity. Furthermore, the coating exhibited excellent tolerance to different pH environments, ranging from strong acid (pH = 1) to strong base (pH = 14). There is no obvious fluctuation of the CAs as the pH values changes, and the droplets remain spherical with CAs larger than 150° , as shown in Figure 7b, which was attributed to excellent chemical stability of the LDIP materials.

Figure 7 (a) WCAs of the LDIP coated surface after different weeks of exposure to air (0, 4, 8, 12, 16, 20, 24 weeks); (b) CAs of water with different pH values from 1 to 14 on the LDIP coated surface.

Figure 8 (a) BSA absorption and bacterial adhesion of LDIP uncoated surface and LDIP coated surface; (b) IC₅₀ of LDIP coated surface.

The formation of biofilm on the material surface is also a major issue for waste water treatment. Once the biofilms have been formed on the material surface, they are extremely hard to remove and show great resistance to a great variety of biocides. As a result, the most extended strategy to prevent infection and material deterioration is to prevent the biofilm formation. Two effective approaches, repelling and killing, are most used [34]. It is well accepted that the micro/nanoscale surface topographical features can play a key role in controlling protein and bacterial attachment. In the present study, the antifouling property of the LDIP coating was investigated using a BSA assay, and the amount of adsorbed protein was quantified using the BCA method. The pristine aluminum foil surface adsorbed 0.51 μg/cm² of BSA, while the LDIP coated surface adsorbed only 0.10 μg/cm² of BSA (Figure 8a). This 80% of reduction comparing to pristine aluminum foil was attribute to superhydrophobicity of LDIP. The antibacterial adhesive property of LDIP coated surface against *E. coil* was also investigated here. There were many *E. coil* cells adhered to the pristine aluminum foil surface after 24h culture, in contrast, the number of adherent bacteria reduced greatly on LDIP coated surface (Figure 8a). Hence, LDIP coated surface exhibited good antifouling/antibacterial properties because of its particular surface chemical composition and “litchi” micro/nanoscale surface hierarchical structure This LDIP coated surface is resistant to biofilm formation, which has very promising applications

for the places like water-treatment plants, oil-drilling operations, hospitals and the ocean applications like underwater pipes that are sensitive to fouling.

Biocompatibility is an important factor for evaluating the potential use of biomaterials, so we investigated the LDIP toxicity here as well (IC₅₀: concentration which reduces cell population by 50% with respect to control) by *in vitro* MTT assay to detect the viability of 3T3 mouse fibroblast cells. To our delight, LDIP was non-toxic towards 3T3 fibroblast cell line (almost a 100% cell viability was observed at 8, 16, 32, 64, 128, 256 and 512 µg/mL, see Figure 8b).

4. Conclusion

In this study, we have demonstrated the fabrication of superhydrophobic carbon material – LDIP by a simple, catalyst-free CVD method. The designed novel LDIP coating surface showed high water repellency and low water adhesion with WCA of 160° and SA of 2.8°, respectively, due to the synergistic effect of low surface energy of carbon and “litchi” micro/nanoscale surface hierarchical structure. The superhydrophobic LDIP possessed excellent self-cleaning property, durability and chemical stability. The membrane made of LDIP powder for oil-water separation exhibited good separation efficiency and reusability. Moreover, bio-test results showed that LDIP coating surface had not only good antifouling/antibacterial properties but also good biocompatibility. The fabrication technique is facile, low-cost and environment-friendly, and the superhydrophobic LDIP offers the great potential in the treatment of oil-pollution and biomedical field.

Appendix A. Supplementary data

Supplementary data related to this article is provided.

Acknowledgements

The authors would like to gratefully acknowledge the Hunan Provincial Natural Science Foundation of China for Award No. 2018JJ3530 for supporting this research.

References

- [1] A. Oberlin. Pyrocarbons. *Carbon* 2002; 40(1): 7-24.
- [2] J.F. Wu, S. Bai, S.H. Liu, H.J. Xu, H.M. Cheng. Fabrication and characterization of large isotropic pyrolytic carbons. *New Carbon materials* 2006; 21(2): 119-124.
- [3] B. Kwiecińska, S. Pusz. Pyrolytic carbon—definition, classification and occurrence. *International Journal of Coal Geology* 2016; 163: 1-7.
- [4] L. Xu, J.F. Wu, S. Bai. Fabrication and microstructure of boron-doped isotropic pyrolytic carbon. *Carbon* 2012; 50(12): 4705-4710.
- [5] M.H. Kim, J.Y. Lee. The primary factors which determine the microstructures of pyrolytic carbons deposited in a tumbling bed. *Journal of Materials Science* 1987; 22(11): 3983-3988.
- [6] D.S. Zhang, K.Z. Li, H.J. Li, Y. Jia, L.J. Guo, H.L. Li. Coefficients of thermal expansion of low texture and isotropic pyrocarbon deposited on stationary substrates. *Materials Letters* 2012; 68(2): 68-70.
- [7] Q. Song, K.Z. Li, H.J. Li, S.Y. Zhang, L.H. Qi, Q.G. Fu. A novel method to fabricate isotropic pyrocarbon by densifying a multi-walled carbon nanotube perform by fixed-bed chemical vapor deposition. *Carbon* 2012; 59: 547-550.
- [8] S.T. Wang, L. Jiang. Definition of superhydrophobic states. *Advanced Materials* 2007; 19(21): 3423-3424.
- [9] E. Vazirinasab, R. Jafari, G. Momen. Application of superhydrophobic coatings as a corrosion barrier: a review. *Surface & Coating Technology* 2018; 341: 40-56.
- [10] Z.X. Xue, Y.Z. Cao, N. Liu, L. Feng, L. Jiang. Special wettable materials for oil/water separation. *Journal of Materials Chemistry A* 2014; 2(8): 2445-2460.
- [11] J.L. Yong, F. Chen, Q. Yang, J.L. Huo, X. Hou. Superoleophobic surfaces. *Chemical Society Reviews* 2017; 46(14): 4168-4217.
- [12] B. Balu, V. Breedveld, D.W. Hess. Fabrication of “roll-off” and “sticky” superhydrophobic cellulose surfaces via plasma processing. *Langmuir* 2008; 24(9): 4785-4790.

- [13] M.N. Qu, G.Y. Zhao, Q. Wang, X.P. Cao, J.Y. Zhang. Fabrication of superhydrophobic surfaces by a Pt nanowire array on Ti/Si substrates. *Nanotechnology* 2008; 19(5): 055707.
- [14] W.C. Wu, M. Chen, S. Liang, X.L. Wang, J.M. Chen, F. Zhou. Superhydrophobic surface from Cu-Zn alloy by one step O₂ concentration dependent etching. *Journal of Colloid and Interface Science* 2018; 326(2): 478-482.
- [15] Y. Hu, C.Y. Huang, D. Su, Q.W. Jiang. Fabrication and characterization of a cotton candy like surface with superhydrophobicity. *Applied Surface Science* 2011; 257(14): 6044-6048.
- [16] D.W. Jeong, U.H. Shin, J.H. Kim, S.H. Kim, H.W. Lee, J.M. Kim. Stable hierarchical superhydrophobic surfaces based on vertically aligned carbon nanotube forests modified with conformal silicone coating. *Carbon* 2014; 79(1): 442-449.
- [17] J.M. Wang, L.D. Wang, L. Feng. One-step fabrication of fluoropolymer transparent films with superhydrophobicity by dry method. *Journal of Applied Polymer Science* 2011; 120(1): 524-529.
- [18] R. Jafari, M. Farzaneh. Fabrication of superhydrophobic nanostructured surface on aluminum alloy. *Applied Physics A* 2011; 102(1): 195-199.
- [19] X.J. Su, H.Q. Li, X.J. Lai, L. Zhang, J. Wang, X.F. Liao, et al. Vapor-liquid sol-gel approach to fabricating highly durable and robust superhydrophobic polydimethylsiloxane@silica surface on polyester textile for oil-water separation. *Applied Materials & Interfaces* 2017, 9(33): 28089-28099.
- [20] L. Zhang, H.Q. Li, X.J. Lai, X.J. Su, T. Liang, X.Z. Zeng. Thiolated graphene-based superhydrophobic sponges for oil-water separation. *Chemical Engineering Journal* 2017, 316: 736-743.
- [21] L. Shen, H.L. Ding, Q.H. Cao, W.C. Jia, W. Wang, Q.P. Guo. Fabrication of ketjen black-high density polyethylene superhydrophobic conductive surfaces. *Carbon* 2012; 50 (11): 4284-4290.
- [22] Y.M. Liu, J.W. Chen, D.W. Guo, M.Y. Cao, L. Jiang. Floatable, self-cleaning and carbon-black-based superhydrophobic gauze for the solar evaporation enhancement at

the air-water interface. *ACS Applied Materials & Interfaces* 2015; 7(24): 13645-13652.

[23] K.D. Esmeryan, C.E. Castano, A.H. Bressler, M. Abolghasemibizaki, R. Mohammadi. Rapid synthesis of inherently robust and stable superhydrophobic carbon soot coatings. *Applied Surface Science* 2016; 369: 341-347.

[24] L. Feng, Z.L. Yang, J. Zhai, Y.L. Song, B.Q. Liu, Y.M. Ma, et al. Superhydrophobicity of nanostructured carbon films in a wide range of pH values. *Angewandte Chemie International Edition* 2003; 42(35): 4217-4220.

[25] P.W. Wang, T.Y. Zhao, R.X. Bian, G.Y. Wang, H. Liu. Robust superhydrophobic carbon nanotube films with lotus leaf mimetic multiscale hierarchical structures. *ACS Nano* 2017; 11(12): 12385-12391.

[26] X.J. Su, H.Q. Li, X.J. Lai, Z.P. Yang, Z.H. Chen, W.J. Wu, et al. Vacuum-assisted layer-by-layer superhydrophobic carbon nanotubes films with electrothermal and photothermal effects for deicing and controllable manipulation. *Journal of Materials Chemistry A* 2018; 6(35):1-10.

[27] S.B. Liu, T. Y. Helen Zeng, M. Hofmann, E. Burcombe, J. Wei, R.R. Jiang, et al. Antibacterial activity of graphite, graphite oxide, graphene oxide and reduced graphene oxide: membrane and oxidative. *ACS Nano* 2011; 5(9): 6971-6980.

[28] R. Das, Md.E. Ali, S.B.A. Hamid, S. Ramakrishna, Z.Z. Chowdhury. Carbon nanotube membranes for water purification: A bright future in water desalination. *Desalination* 2014; 336: 97-109.

[29] R.X. Tan, Z.Q. Fan, Z.Y. Xie, M.Y. Zhang, K.J. He, Q.Z. Huang. Fabrication of large-sized high density bulk isotropic pyrocarbon materials of a special composite microstructure by fixed-bed chemical vapor deposition. *Carbon* 2016; 101: 439-448.

[30] R.E. Brown, K.L. Jarvis, K.J. Hyland. Protein measurement using bicinchoninic acid: elimination of interfering substances. *Analytical Biochemistry* 1989; 180(1): 136-139.

[31] H. Schulz, M. Leonhardt, H-J. Scheibe, B. Schultrich. Ultra hydrophobic wetting behavior of amorphous carbon films. *Surface & Coating Technology* 2005; 200(1-4): 1123-1126.

- [32] X.J. Su, H.Q. Li, X.J. Lai, L. Zhang, X.F. Liao, J. Wang, et al. Dual-functional superhydrophobic textile with asymmetric roll-down/pinned states for water droplet transportation and oil-water separation. *Applied Materials & Interfaces* 2018, 10(4): 4213-4221.
- [33] A. Pozzato, S. Dal Zilio, G. Fois, D. Vendramin, G. Mistura, M. Belotti, et al. Superhydrophobic surfaces fabricated by nanoimprint lithography. *Microelectron Engineering* 2006; 83(4): 884–888.
- [34] F. Siedenbiedel and J.C. Tiller. Antimicrobial polymers in solution and on surfaces: overview and functional principles. *Polymers* 2012; 4(1): 46-71.