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A biomimetic 3D ordered multimodal porous carbon with hydrophobicity for oil–water separation

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ABSTRACT

We present a dual-templating method to synthesize a biomimetic 3D ordered multimodal porous carbon (3DOMPC) using the phenolic resol as a carbon source and the amphiphilic triblock copolymer surfactant (F127) as the mesopore-generating agent on the polystyrene colloidal crystal scaffold. The biomimetic 3DOMPC shows the brilliant structural color originating from the periodical, hierarchical ordered porous structure. More importantly, the resulting 3DOMPC exhibits hydrophobicity (water contact angle, 120°) and superoleophilicity (oil contact angle, 0°) with high oil absorption capacity, which can effectively and selectively collect oil from water surface, providing a potential candidate to the traditional oil-absorbent materials for the oil–water separation.

1. Introduction

Biologically inspired design, adaptation, or derivation from nature is referred to as “biomimetics”. Some biological surfaces have revealed many unusual properties. One typical example is the brilliant blue color of the Morpho butterfly arising from the surface with periodic structure in micro- and nanoscales on its wings [1]. Besides the brilliant structural color, another interesting phenomenon, known as hydrophobicity, has also drawn much attention. The wings of the Morpho butterfly can act as the waterproof layer to prevent water from penetrating its wings due to the ordered microstructure of the wings' surfaces [2]. Three-dimensionally ordered macroporous (3DOM) materials are one kind of artificial materials with spatially ordered lattices that exhibit brilliant structural color. Song reported that 3DOM carbon with oil contact angle of $3.8 \pm 1.3^\circ$ was ascribed to the oleophilic property of carbon and the rough macroporous structure of 3DOM carbon [3].

The wettability of a solid surface is a very important property depending on both chemical composition and surface structure. Li and Cai fabricated the hierarchical porous silica film with orderly arranged macropores/disordered mesopores in the skeleton. However, it was found superhydrophilicity with water contact angle of $5 \pm 1^\circ$ [4]. In this work, we present a dual-templating method to synthesize a biomimetic 3D ordered multimodal porous carbon (3DOMPC). The brilliant structural color of 3DOMPC reveals the hydrophobic and superoleophilic properties without the modification of low surface energy. Therefore, it can effectively and selectively absorb oil from water surface, which indicates the potential to be used in the oil–water separation field instead of traditional oil-absorbent.

2. Experimental details

Polystyrene (PS) spheres were synthesized by the emulsifier-free emulsion polymerization, as previously described [5]. The PS colloidal crystal (CC) templates were fabricated following the centrifugal deposition. The phenolic resol was prepared from phenol and formaldehyde according to a basic polymerization method [6]. For the infiltration process, 1.0 g of PS CC templates were immersed in a homogenous solution including F127 (0.5 g, Sigma-Aldrich), resol (2.0 g, 50 wt%), and ethanol (2.5 g) for 24 h at 25 °C. The precursor-filled templates were dried at 100 °C for 24 h and pyrolyzed at 450 °C for 3 h, and 900 °C for 2 h under flowing N_2 with a heating rate of 1 °C/min to form the product of 3DOMPC. In contrast, 3DOM carbon was fabricated using the similar procedure without additive F127.

The structure of 3DOMPC was investigated by SEM (Hitachi S-4800) and TEM (JEOL JEM-2100). The pore structure was analyzed by nitrogen sorption experiments (Micromeritics ASAP 2020). Thermogravimetric (TG) analysis was performed on a BOIF WCT-II analyzer. Fourier transform infrared (FT-IR) spectra were collected on a Nexus spectrometer (Nicolet, USA) using KBr disks. The wettability of samples was measured with an optical contact angle measuring device (KRUSS DSA-100).

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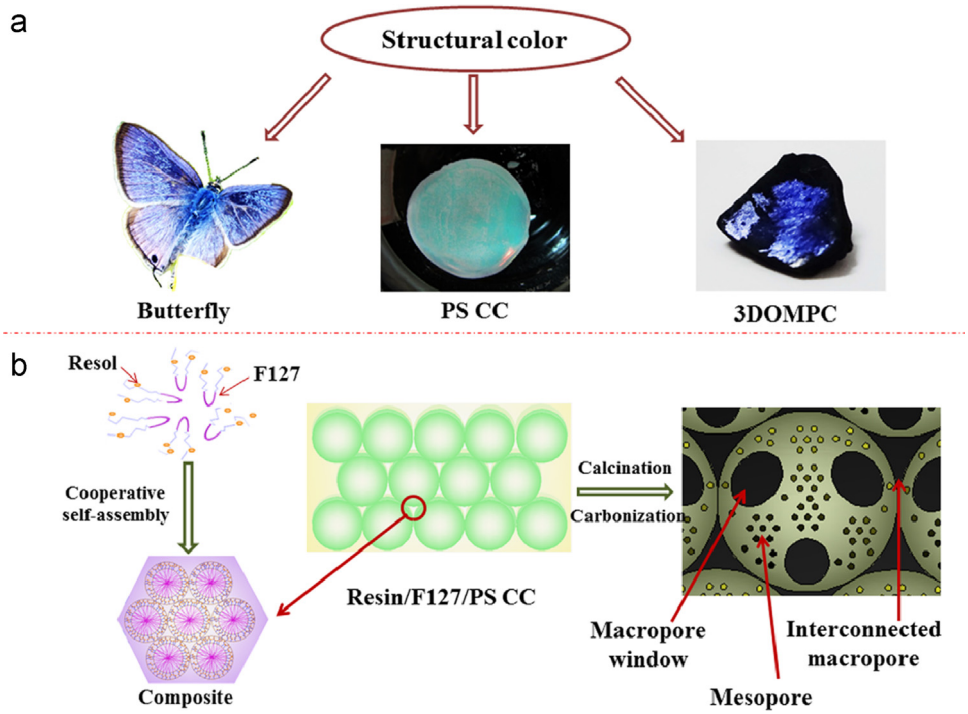

Fig. 1. (a) Photos of samples with structural color; (b) Scheme for the preparation of 3DOMPC by one dual-templating method. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

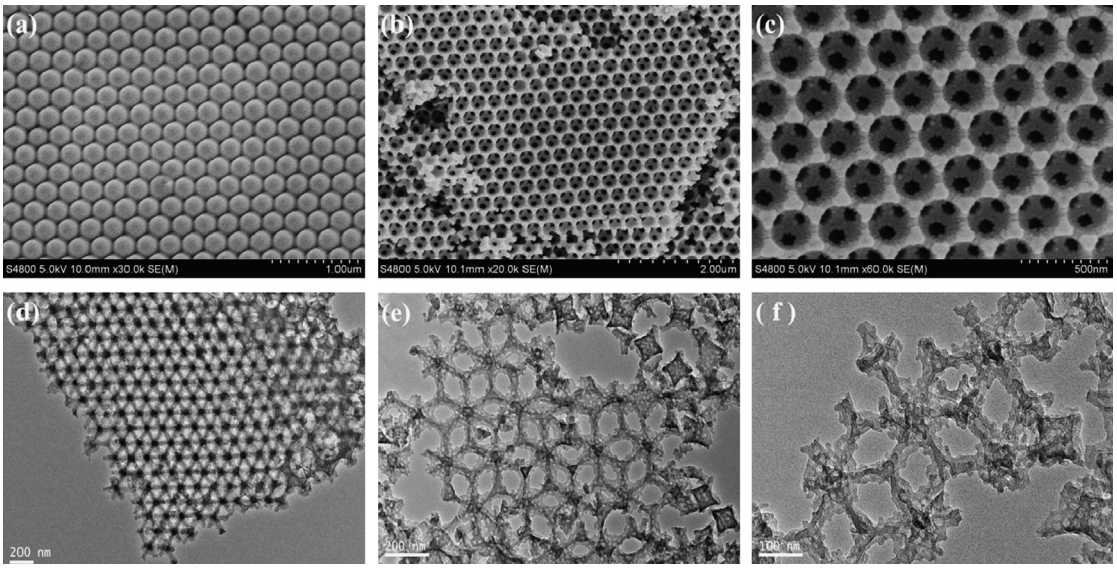

Fig. 2. SEM images of (a) PS CC and (b) and (c) 3DOMPC, and TEM images of (d)–(f) 3DOMPC.

3. Results and discussion

The structural color of the butterfly and samples is illustrated in Fig. 1a. The brilliant blue color of PS CC and 3DOMPC mainly originated from their periodical, ordered pore structure, resulting from the diffraction and interference effect of light between air and the microstructure surfaces. Fig. 1b schematically shows the fabrication method of 3DOMPC using the dual-templating technique. The orderly arranged macropores were obtained by the sacrificial PS CC template and the formation of the ordered mesopores was related to a possible cooperative self-assembly. During the evaporation induced self-assembly, the resol cooperatively polymerized around amphiphilic triblock copolymer micelle, further leading to the composite [7]. The phenolic resin was stabilized by the heat treatment during the removal of triblock copolymer and PS CC, and then the macro-/mesopore structure was formed after calcination. Eventually, 3DOMPC was obtained during carbonization process in the nitrogen atmosphere.

Fig. 2a–c represent the SEM images of samples. The PS CC with uniform particle diameter at 265 nm, showed a close-packed face-centered-cubic (fcc) lattice with the (1 1 1) facet (Fig. 2a). After removal of templates, the interconnected framework of 3DOMPC was composing of macropores and the macropore windows (Fig. 2b and c). The macropore diameter was 221 nm, suggesting

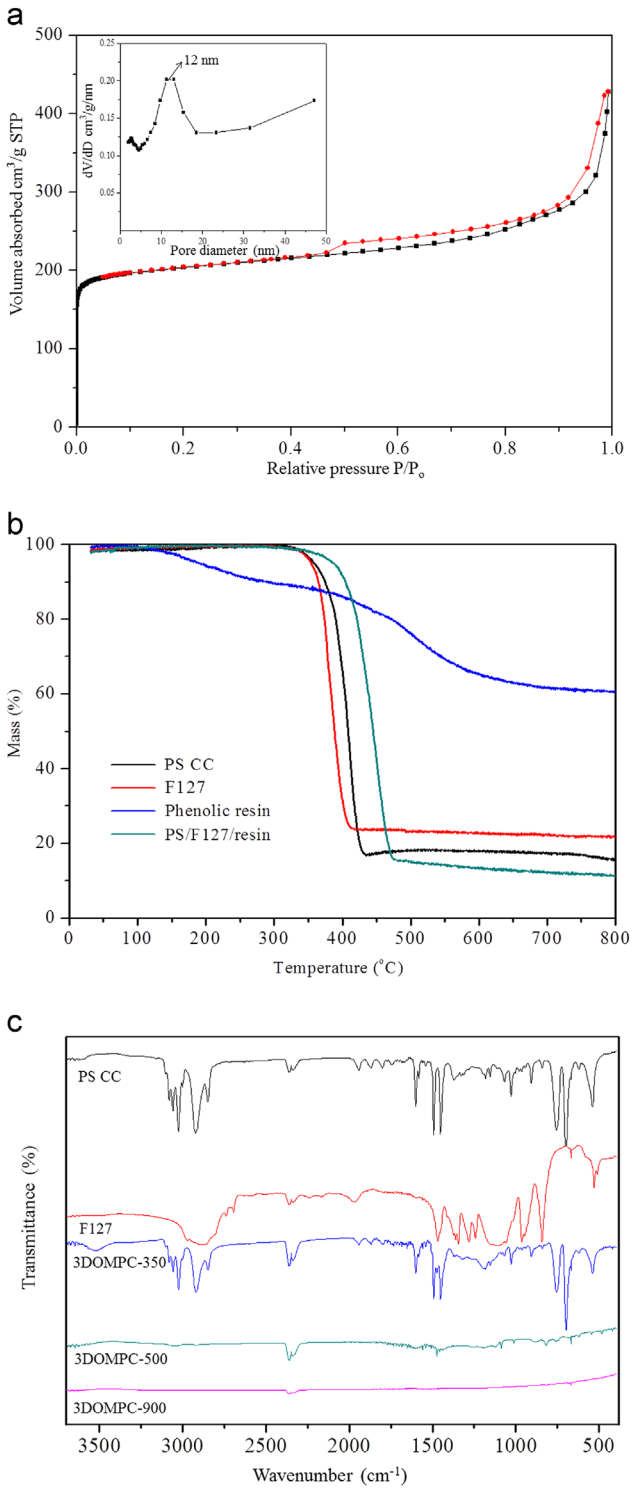

Fig. 3. (a) N_2 adsorption – desorption isotherms and pore size distribution curve of 3DOMPC; (b) TG analysis curves and (c) FT-IR spectra of samples.

the shrinkage of framework (16%). The macropore window with diameter at 74 nm was attributed to the contact areas between neighboring PS spheres during the heating treatment of PS CC. The TEM images of 3DOMPC show the hierarchical ordered porous structure (Fig. 2d–f). The mesopores of the average diameter of about 12 nm demonstrated that the dual-templating method could be used to successfully fabricate the ordered multimodal porous architecture.

N_2 sorption isotherms of 3DOMPC exhibited type IV curve with a hysteresis loop at $P/P_o = 0.45 - 0.85$, suggesting the presence of mesopore (Fig. 3a). A narrow pore size distribution with a mean value of 12 nm was calculated from the adsorption branch according to the BJH model. The BET surface area was 753 m^2/g and the pore volume was 0.58 cm^3/g. The TG curves of samples under N_2 revealed that the PS and F127 templates were early decomposed at 390–410 °C and the nearly complete combustion was observed at 420–430 °C (Fig. 3b). Therefore, the phenolic resin can be used to the supporting and confining scaffold for the inorganic phase. The FT-IR spectra of samples explained the intermediate structure during the pyrolysis process (Fig. 3c). The band at 3100–2800 cm^{-1}, 1450–1650 cm^{-1}, 1100 cm^{-1} and 690–800 cm^{-1} could be attributed to the C–H stretching bands of PS and F127. After calcination at 350 °C under N_2, the bands at 1100 cm^{-1} and 2800–3000 cm^{-1} almost disappeared, implying the decomposition of the templates. The spectra of 3DOMPC-500 and 3DOMPC-900 demonstrated the reduced relative intensity of all characteristic bands until complete disappearance.

Fig. 4a shows the wettability of 3DOMPC and 3DOM carbon. It was found that the 3DOMPC exhibited strong hydrophobic and superolephilic properties, as indicated by water contact angle of about 120° and oil contact angle of about 0°. The wettability of the solid is mainly determined by the average free energy per unit area beneath the droplet, and the roughness coefficient of the solid's surface [8]. The hierarchical porous structure of 3DOMPC could obviously reduce the surface free energy, leading to the low surface tension of water droplet by keeping a spherical shape [9]. In contrast, the water contact angle of 3DOM carbon is only about 65°. It clearly demonstrated that rough surface of 3DOMPC contributed greatly to the hydrophobic property on the basis of the Wenzel's equation [10]. On the contrary, the oil droplet can immediately spread on the biomimetic 3DOMPC surface. This was ascribed to the oleophilic property of carbon and the rough porous structure of 3DOMPC, according to the Cassie–Baxter law [11].

To investigate the absorbency of 3DOMPC, we employed paraffin oil in this experiment. When the 3DOMPC is immersed in water, it does not absorb water. The 3DOMPC revealed that the absorption capacity reached up to 1.5 times its weight when it dipped into the pure paraffin oil for a few seconds. To better verify the 3DOMPC's practical application, Fig. 4b illustrates the detailed process of oil absorption by a typical 3DOMPC sample. The results showed that the paraffin oil on the water surface can be completely absorbed into the 3DOMPC within a few seconds. It is important for 3DOMPC to remain floating after the collection of oil from the water surface, because the high buoyancy of 3DOMPC is helpful for oil sorption and removal from the spilled area [12]. The biomimetic 3DOMPC tends to drift on the remaining area of the oil due to its water-repelling and oil-wetting properties, which leads to a unique floating-and-cleaning capability that is particularly useful for oil–water separation.

4. Conclusions

The biomimetic 3D ordered multimodal porous carbon was fabricated by one dual-templating method with the PS colloidal crystal and the triblock copolymer F127 as templates, while phenolic resol as a carbon source. On the basis of the hierarchical ordered porous structure, the biomimetic 3DOMPC exhibited the blue structural color, high BET surface area (753 m^2/g), strong hydrophobicity (water contact angle, 120°) and superoleophilicity (oil contact angle, 0°). The results suggest that the biomimetic 3DOMPC can selectively collect oil from water surface, showing the absorption capacity of 1.5 g/g for paraffin oil. The excellent selectivity and good floating ability of the biomimetic 3DOMPC

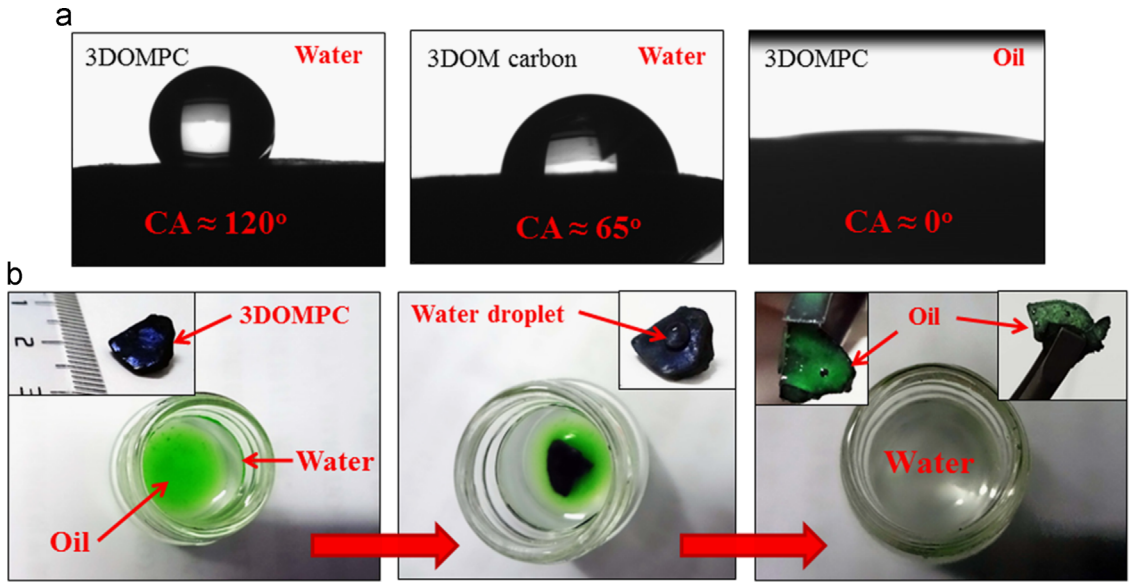

Fig. 4. (a) The wettability of 3DOMPC and 3DOM carbon. (b) Removal of paraffin oil from water surface by a typical 3DOMPC sample. The paraffin oil was dyed with oil color for clear observation.

make it a promising candidate of traditional oil-absorbent for the oil–water separation.

Acknowledgments

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