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Full Length Article

Template-free synthesis of multifunctional carbonaceous microcone forests

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ABSTRACT

Forests of vertically aligned carbonaceous microcones are fabricated directly on a nickel mesh by microwave-plasma-assisted chemical vapor deposition. The microstructure is formed through a simple one-step process involving self-assembly. The fabricated composite exhibits superhydrophobicity and superoleophilicity as well as low density, owing to which it floats on water and can be used for the in-situ separation of oil from water at the oil/water interface. Furthermore, the composite exhibits pH responsivity, and its water permeability can be varied simply by altering the pH of the aqueous solution. In addition, the composite is suitable for use as an electrode material for supercapacitors owing to its large geometric surface area, porous structure, and superior electrical properties, which allow for fast ion and electron transportation. Thus, this composite consisting of forests of vertically aligned carbonaceous microcones on a nickel mesh is expected to find use in a wide range of fields and applications, including in environmental cleanup, flow switches, and energy storage devices.

1. Introduction

Nanostructured carbon materials, such as carbon nanotubes (CNTs) [1], fullerenes [2], graphene [3], porous carbon [4], and carbon nanofibers [5], have attracted the attention of scientists and engineers owing to their electrical [6], optical [7], catalytic [8], mechanical [9], and thermal properties [10], which make them suitable for many applications. As a result, these materials are being used extensively as electrode materials for batteries [11], fuel cells [12], and supercapacitors [13]; for gas storage [14]; and as supports in several catalytic processes [15]. The recent focus on the synthesis of carbon nanomaterials has resulted in the development of various highly ordered carbon nanostructures as well as their composites [16–19]. The attributes of these materials are both relevant to their ordered nanostructures and the fundamental properties of carbon. Several ordered carbon nanomaterials have been reported recently, such as ordered carbon clusters [20], ordered carbon-based nanospheres [21], CNT sheets [22], and forests of vertically aligned CNTs [23]. However, the processes for synthesizing these materials have their own drawbacks in terms of complexity, cost efficiency, and environmental friendliness, which dramatically limits the applicability of these materials [24,25]. Therefore, the development of facile, environmentally friendly, and low-cost methods for fabricating different types of highly ordered carbon micro/nanostructures would be desirable.

As is known to all, energy independence and environmental pollution and, in particular, water and air pollution from the burning of fossil fuels, are the two most pressing problems that society is facing today [26]. Considerable efforts are being devoted to preventing pollution related to oil. Oily sewage is inevitably a part of industrial and domestic sewage, and chemical spillages also occur frequently. Hence, there is an urgent need for methods that allow for the effective separation of oil and water and thus can be used for cleaning oil spills [27]. The separation of oil and water remains a considerable challenge because conventional separation methods exhibit several shortcomings. They are intricate, have low efficiencies, are expensive to perform, and result in the generation of secondary pollutants [28]. Numerous studies have confirmed that porous materials with superhydrophobicity and superoleophilicity exhibit superior performance with respect to water/oil separation, given their special wettability properties. Owing to these properties, they can resist water but allow the permeation of various

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types of oils [29,30]. However, most of the materials investigated for oil/water separation cannot be used for the in-situ removal and collection of oil. In addition, although some materials that can absorb oil from the polluted water zone in situ and in a selective manner have been reported, purifying these oil absorbents is so difficult that it results in secondary pollution and limits the applicability of these materials [31]. Further, the urgent demand to replace fossil fuels has stimulated intensive research on energy storage and conversion during the past decades. Supercapacitors, which are promising energy storage devices, have aroused much research interest because of their high power density and excellent cycling stability compared with conventional battery [32,33]. However, the development and fabrication of new electrode materials that show energy and power densities high enough to meet the requirements of efficient energy storage and conversion devices remains a challenge.

In this paper, we present a facile method for the fabrication of forests of uniformly ordered, vertically aligned carbonaceous microcones on a nickel mesh substrate by microwave-plasma-assisted chemical vapor deposition (MPACVD). The hierarchical structure with microscale pores exhibits enhanced hydrophobicity and oleophilicity without requiring any additional chemical surface modification treatment. Further, the as-prepared functionally integrated mesh with enhanced wettability properties can float on water and in situ separate oil from water at the oil/water interface. In addition, the fabricated composite is also suitable for use as a supercapacitor electrode material owing to its ordered nanoporous structure, and the fundamental electrical properties of carbon, which allow for fast ion and electron transportation. Thus, the ordered carbonaceous microcones fabricated in this study through a self-assembly process should find use in a wide range of applications in the fields of environment and energy management, including in environmental cleanup, flow switches, and energy storage devices.

2. Experimental

2.1. Materials used

Commercial nickel meshes with sizes of 50–400 were obtained commercially in Harbin, China. The meshes sizes were defined based on the number of pores per 25.4 mm. Deionized water (Aladdin Industrial Inc) was used for all the experiments. Hydrochloric acid (analytical grade) was obtained from Beijing Chemical Works and diluted in the laboratory. Acetone and ethanol were purchased from Beijing Chemical Works and used without modification. N_2 (3N), H_2 (5N), and CH_4 (5N) were purchased from Harbin Liming Co Ltd. and used without modification. Different types of oils, such as diesel oil, olive oil, liquid paraffin, and cooking oil, were obtained commercially from the market in Harbin. The fat-soluble dye oil red O (ORO) was purchased from Aladdin Industrial Inc and used for dyeing the diesel oil sample.

2.2. Synthesis of forests of vertically aligned carbonaceous microcones

Forests of vertically aligned carbonaceous microcones were synthesized directly on the nickel mesh substrates by MPACVD without using any complex processes. First, the nickel meshes were soaked in diluted hydrochloric acid (5% vol) to remove the surface NiO coating. They were then cleaned with deionized water and dried with N_2. Next, the nickel meshes were cleaned with acetone, ethanol, and deionized water and dried with N_2. The nickel meshes were then heated directly using a hydrogen plasma in the vacuum chamber of the MPACVD system; no other heating source was employed. The sample temperature was measured using an infrared temperature measurement system. The process consisted of the following three steps. First, the nickel mesh in question was heated to 800 °C by the hydrogen plasma in a flow of H_2 (200 sccm) at a pressure of 120 mbar for 1 min. Next, a power of 2500 W, H_2/CH_4 flow rate ratio of 160/40 sccm, and temperature/pressure of 580 °C/60 mbar were used to grow microcones on the nickel mesh for 3 min. Finally, the sample was cooled rapidly to room temperature in the CVD chamber in an atmosphere of N_2.

2.3. Sample characterization

The surface morphologies of the specimens were examined using a scanning electron microscopy system (SEM) (Helios Nanolab 660i, FEI), which was operated at 1–20 kV. The surface morphologies and microstructures were also investigated using a transmission electron microscopy (TEM) system (Tecnai G2 F30, FEI) operated at 300 kV. For the TEM imaging process, the carbonaceous microcone forests were scratched from typical specimens and dispersed by ultrasonic dispersion. A Raman microscope (Lab RAM HR800, Horiba Jobin–Yvon) with a 458-nm laser was also used to characterize the specimens under ambient conditions. The wettabilities of the specimens were measured using an OCA20 system (Data-Physics) under ambient conditions. The water contact angle (WCA) values were taken as the average of the measurements performed at five different areas on each specimen. Optical images of the specimens were taken using a Nikon D7100 camera.

3. Results and discussion

A schematic illustration of the process for fabricating the forests of vertically aligned carbonaceous microcones is shown in Fig. 1(a). It shows that the catalytic particals were crucially important for microcone growth. The morphology of an untreated nickel mesh is shown in Fig. 1(b). It can be seen that the surface of the nickel mesh is relatively smooth and contains only a few minor flaws. Compared to the surface of the untreated mesh, that of the mesh sample treated with the hydrogen plasma is extremely rough and coated with a large number of catalyst particles (see Fig. 1(c)). When methane was introduced into the reaction system, these catalytic particles interacted with the hydrocarbon ions, resulting in the formation of the carbonaceous microcones. Fig. 1(d) shows the morphology of the microcones synthesized on a nickel mesh wire. It can be seen that the nickel mesh wire is evenly coated with an array of vertically aligned microcone pillars. Therefore, it can be concluded that forests of highly ordered, vertically aligned microcones were successfully synthesized on the nickel mesh substrates by a simple, economical, and environmentally friendly self-assembly process.

Images of a typical forest of vertically aligned microcones grown on a nickel mesh are shown in Fig. 2. The images in Fig. 2(a) and (b) are SEM images of the sample. It can be seen that the nickel mesh wires are evenly covered by the vertically aligned microcones, with the dimensions of the openings of the mesh being greater than $50 \times 50\ \mu m$. The large pore or opening size ensured that the fabricated composite exhibited high flux. Further, the pores did not get blocked readily when the composite was used for separating oil from water. Fig. 2(c) shows a top view of the vertically aligned microcones on a nickel mesh, while Fig. 2(d) shows a cross-sectional view of the microcone forest. It can be seen clearly that the height of the microcones is approximately 2 μm and their radius in the middle is approximately 500 nm. Fig. 2(e) shows that dense, hair-like nanofibers are distributed on the surfaces of the microcones, giving the microcones a pine-tree-like appearance. Further, several dark nanospheres are encapsulated within the microcones (see Fig. 2(f)).