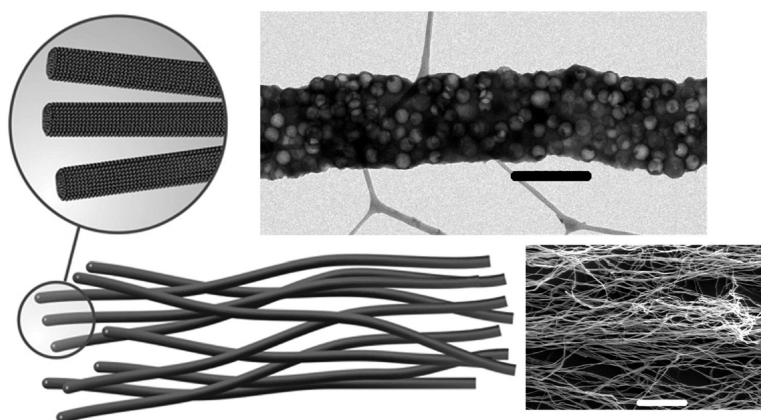Communication

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Porous Carbon and Carbon/Metal Oxide Microfibers with Well-Controlled Pore Structure and Interface

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Over the past few decades, the development of carbon materials of various forms and sizes including fullerenes, carbon nanotubes, carbon fibers, carbon aerogels, and carbon nanoparticles has attracted considerable attention because of their unique structural and opto-electric properties.[1] Dispersion of a catalytic-active or redox-active transition metal oxide throughout a high-surface-area carbon support has been reported to enhance catalyst performance and electrochemical capacitor response.[2] When considering the utilization of carbon materials in catalysis, electrochemical energy storage, and gas or liquid separations and storage, a simple and effective technique for creating porous carbon with both large surface area and incorporated functional components in a controllable fashion is needed.

One-dimensional porous carbon fibers and carbon/metal oxide composite fibers with well-controlled pore structures and carbon—metal oxide interfaces are desired for many applications. Porous carbon fibers have been fabricated previously, using conventional extrusion methods,[3] electrospinning,[4] or template synthesis.[5] The resulting fibrous carbon materials, however, usually have pores that are randomly dispersed in the carbon matrix with pore sizes that are not uniformly tunable over a wide range. Moreover, porous composite carbon/metal oxide fibers with controllable carbon—metal oxide interfaces have not yet been reported. Here we report a large-scale and versatile synthetic approach for obtaining porous carbon and porous carbon/hollow metal oxide microfibers with uniform and tunable pore sizes (50–400 nm) and well-defined carbon/metal oxide interfaces by using an ice-templating strategy. Different metal oxides (ZrO_2, TiO_2, γ-Fe_2O_3, etc.) are incorporated into the porous carbon fibers, enabling the manipulation of the composition of the composite fibers and their catalytic, electrochemical, and optical properties.

The ice-templating strategy has been developed to produce nonporous inorganic fibers and aligned porous inorganic or polymer monolithic structures.[6] In this study, the overall microscopically defined fibrous morphology is templated from ice crystals in the form of very high aspect ratio platelets grown during freezing. The ice crystals expel the solutes, which are originally homogeneously dispersed in the aqueous gel, from the forming ice phase and entrap them within the directed channels between the ice crystals.

In order to generate uniform and tunable pores within the carbon fibers, monodisperse spherical SiO_2 particles with tunable sizes (50–400 nm) were employed as templates, which were prepared by the well-known Stöber method[7] (100–400 nm) or the reverse emulsion approach (50–100 nm). A layer of metal oxide (MO) was coated onto the SiO_2 particles through a sol–gel approach, followed by growth of a polyacrylonitrile (PAN) shell through
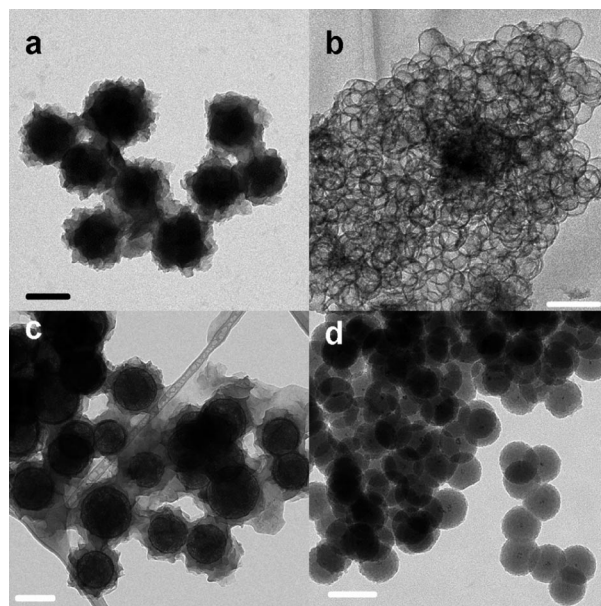

Figure 1. TEM micrographs of (a) SiO_2@PAN particles, (b) hollow carbon capsules, (c) SiO_2@ZrO_2@PAN particles, and (d) γ-Fe_2O_3@SiO_2@C particles. Scale bars: (a−c) 200 nm, (d) 100 nm.

emulsion polymerization process to create a SiO_2@MO@PAN core/shell structure. PAN is a well-known precursor for conventional microsized carbon fibers, which gives a high carbon yield under pyrolysis. A submicrometer scale "brick-and-mortar" assembly approach was developed to assemble these core/shell "bricks" into fibrous structures with assistance of polyvinyl alcohol (PVA) as "mortar" by templating from the high-aspect-ratio ice crystals that form during freezing. The SiO_2@PAN or SiO_2@-MO@PAN core/shell particles were dispersed in a 0.1 wt % PVA (MW ∼ 72 000) aqueous solution and diluted to 0.1–0.5 wt %, followed by freezing in a −80 °C cold bath. The ice was then sublimed by freeze-drying, and scaffolds of interweaved inorganic/polymer composite fiber bundles were produced. The resulting brick-and-mortar composite fibers are composed of closely packed SiO_2@MO@PAN core/shell particles, and the mortar is made of PVA, which serves as an organic glue to hold the bricks together. An oxidative stabilization step was carried out to avoid softening and melting of carbon fibers at higher temperatures by heating the inorganic/PAN fibers in air to 200 °C for 1 h. Afterward, a pyrolysis process was carried out to carbonize the fibers at 800 °C under argon atmosphere, followed by removal of silica cores with concentrated alkali (e.g., 10 M NaOH) to create the porous carbon fiber—hollow sphere composites.

Figure 1a shows a transmission electron microscopy (TEM) micrograph of SiO_2@PAN particles. A core–shell structure with

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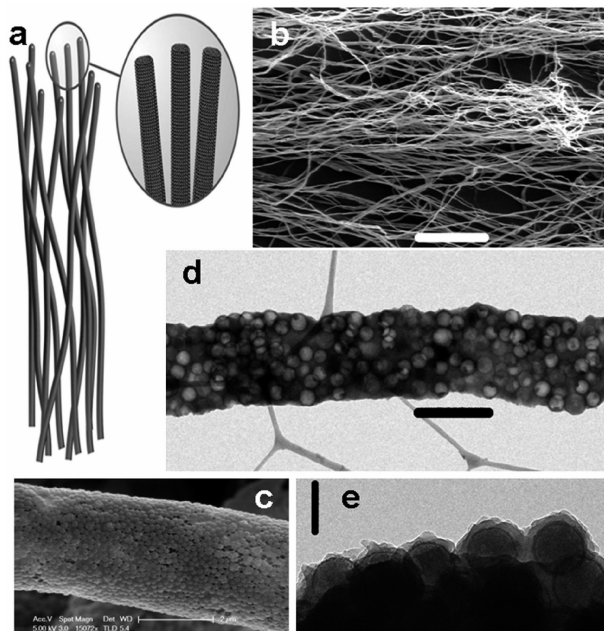§ The Chinese University of Hong Kong.

Figure 2. (a) A schematic representation of porous carbon fibers assembled from uniform hollow carbon or carbon/metal oxide capsules. (b, c) SEM micrographs of SiO_2@PAN fibers under different magnification; TEM micrograph of (d) porous carbon fibers and (e) SiO_2@ZrO_2@PAN fibers. Scale bars: (b) 50 μm, (c,d) 2 μm, (d) 200 nm.

~200 nm silica core and ~40 nm polymeric shell is clearly observed. After pyrolysis and silica removal, hollow carbon capsules are obtained (Figure 1b). The thickness of the carbon shell is ~10 nm, which is made by coating silica nanoparticles with diameters ~80 nm. Nitrogen adsorption/desorption isotherms (Figure S1) exhibit an obvious hysteresis loop over a wide range of relative pressures, and the corresponding pore size distribution (PSD) calculated from the adsorption branch of the nitrogen isotherm by the Barrett–Joyner–Halenda (BJH) method is centered at ~80 nm, consistent with the size of silica templates. The Brunauer–Emmett–Teller (BET) surface area and total pore volume are 1176.8 m^2/g and 2.23 cm^3/g, respectively. Hollow carbon capsules with different sizes can be obtained by using silica cores with tunable diameters as templates.

Layers of other metal oxides can be conveniently incorporated via a sol–gel approach. The TEM image of SiO_2@ZrO_2@PAN particles with clear SiO_2/ZrO_2/PAN interfaces is shown in Figure 1c. After pyrolysis and leaching out the silica cores, hollow ZrO_2@C capsules were created with a ~20 nm ZrO_2 inner shell and ~10 nm carbon outer shell (Figures S2−S4). This sol–gel technique can be extended to a variety of functional metal oxides that have corresponding metal alkoxide precursors. It allows for definitive control of the texture, composition, and homogeneity.

Metal oxide nanoparticles can be incorporated into the hollow carbon capsules, as well. An example of superparamagnetic γ-Fe_2O_3 nanoparticles (NPs) encapsulated as γ-Fe_2O_3@SiO_2@C particles is shown in Figure 1d. Hollow γ-Fe_2O_3@C capsules are formed after selectively leaching out silica (Figure S5). The metal oxide NPs can be easily replaced by metal NPs,[8] giving complex metal NP core/shell structures with controllable composition and interfaces (e.g., hollow Au@MO@C capsules).

The heterogeneous bricks coated with polymeric shells were assembled into a 1D fibrous structure through a PVA-assisted ice-templating approach (Figure 2a). Scanning electron microscopy (SEM) micrographs (Figure 2b,c) of the SiO_2@PAN composite fibers reveal rounded, randomly oriented and interwoven fibers.

They have a constant diameter along the entire length in the range of 1–5 μm, and their lengths vary from hundreds of micrometers to several millimeters. PVA plays an important role in the formation of the fibers. Large, irregular aggregates of hydrophobic SiO_2@PAN particles are formed without PVA. PVA therefore helps to "glue" together the neighboring bricks, leading to stable fibrous structures after freeze-drying. The initial concentration of the particle solution and PVA was found to be crucial for morphology control; freezing a more concentrated particle solution resulted in a mixture of fibers and flakes.

Porous carbon fibers were obtained after leaching out the silica cores (Figures 2d and S6). The nitrogen adsorption isotherm and the corresponding PSD of porous carbon fibers are shown in Figure S7. The resulting isotherm can be classified as a type-V isotherm with type-H3 hysteresis.[9] It exhibits a BET surface area of 345.8 m^2/g and a total pore volume of 1.1 cm^3/g. The corresponding PSD data calculated from the adsorption branch of nitrogen isotherm by the BJH method show that the PSD is narrow and centered at ~180 nm, which is consistent with the faithful replication of silica particles. Other functional metal oxide layers can be incorporated into the fibrous form, as well, for example, SiO_2@ZrO_2@PAN fibers (Figure 2e). Hollow ZrO_2@C fibers in which a layer of ZrO_2 was incorporated at the internal surface of carbon capsules can be obtained when silica cores are removed (Figure S6e).

In summary, porous carbon and carbon/metal oxide microfibers with well-controlled pore structures and interfaces have been successfully prepared by a PVA-assisted ice-templating approach. It is a bottom-up growth approach with control of composition and interface that imparts to the as-produced composite fibers various functions. The results presented here are of technological interest as these porous carbon and carbon/metal oxide composite fibers are promising candidates for a wide range of applications in which fiber morphology, lightweight, and controlled pore structure and interface are strongly desired. This approach is further applicable to different inorganic/organic core/shell building blocks and opens new avenues to the rational design of functional fibrous materials with well-defined inorganic–organic architectures through a bottom-up assembly method.

Supporting Information Available: Experimental details, TEM and SEM micrographs, nitrogen absorption isotherms, and wide-angle X-ray diffraction patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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