Synthesis and Catalytic Applications of Self-Assembled Carbon Nanofoams**

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Template-mediated syntheses have produced novel mesoporous inorganic materials with periodic structures,[1–7] while additional new forms of mesoscopic organic-inorganic hybrid materials have been prepared through the incorporation of organic functional groups into the inorganic framework.[8,9] Mesoporous silica has also been used as a mold to create nanostructured carbon, whose porosity was derived via the removal of the silica mesostructure.[10–16] Herein, we describe the synthesis of a novel form of carbon, termed carbon nanofoam (CNF), which exhibits a high surface area, tunable pore sizes, and electrical conductivity. CNF is derived directly through a surfactant-templated synthesis, bypassing any need for a mesostructured mold. It possesses excellent chemical, mechanical and thermal stabilities, as well as net-shape formability. As a support material, CNF has successfully prevented the undesired agglomeration, particle growth and oxidation of palladium clusters, so that a reusable Heck catalyst could be achieved.

Unlike other nanostructured carbon materials,[17–19] CNF is synthesized from the carbonization of a surfactant-templated carbonaceous precursor. Recently, Liu et al. reported the synthesis of an ordered mesoporous carbon with a cage-like structure by the carbonization of a self-assembled triblock copolymer (Pluronic© F108, $EO_{132}PO_{50}EO_{132}$) and resorcinol-formaldehyde in a non-aqueous solution.[20] Herein, we report a solvent-free, liquid-phase synthesis of a new self-assembled carbon material. Its preparation involves only three simple steps: (i) templating of the carbon precursor, furfuryl alcohol, with a long-chain aliphatic alcohol surfactant to form an ordered mesostructure, (ii) polymerization of the templated carbon precursor by addition of a catalyst, *p*-toluene sulfonic acid, followed by mild curing, and (iii) carbonization of the carbon precursor and removal of the surfactant by heat treatment in an inert atmosphere.

In the CNF synthesis, the long-chain aliphatic alcohol was dissolved in furfuryl alcohol at 60 °C, and then cooled to room temperature to produce a waxy liquid-crystalline solid, which produced birefringence under a cross-polarized optical microscope. Unlike the X-ray diffraction (XRD) patterns of pure aliphatic alcohols, the XRD patterns of solid mixtures of furfuryl alcohol and aliphatic alcohols (at 1:1 weight ratio) exhibited sharp peaks, which corresponded to a well-ordered lamellar mesostructure (see Fig. 1). The XRD patterns of the latter were attributed to the surfactant templating of furfuryl alco-
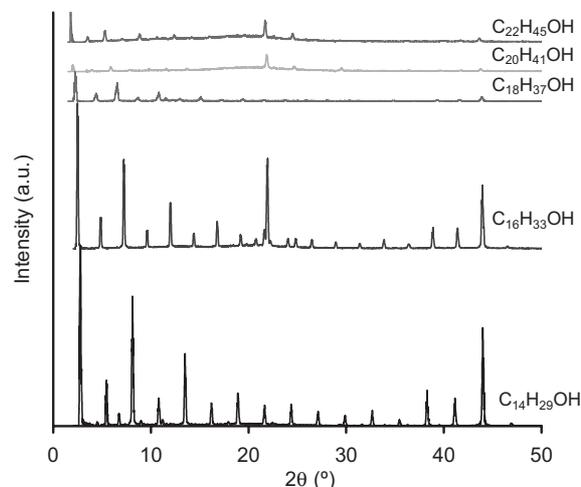
Figure 1. XRD patterns of mixtures of furfuryl alcohol and different aliphatic alcohol surfactants (Siemens D5000 θ–θ X-ray diffractometer).

hol, as the *d* spacing of the lamellar structure was controlled by the choice of surfactant. As the chain length of the aliphatic alcohol was increased from 14 to 22 carbons, the *d* spacing increased systematically from 3.35 to 4.95 nm (see Supporting Information (SI) Table S1).

The mixture of furfuryl alcohol and aliphatic alcohol at 40 °C was subjected to curing through the introduction of a small amount of *p*-toluene sulfonic acid, and was then slowly heated to 120 °C. During this process, the furfuryl alcohol units began to polymerize, losing hydroxyl groups in the form of water, which reduced the interaction between the precursor

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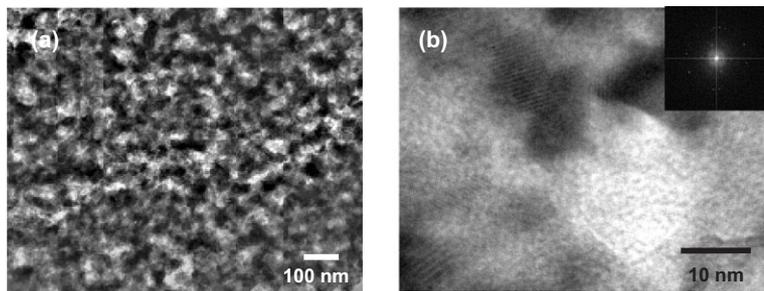E-mail: jyying@ibn.a-star.edu.sg

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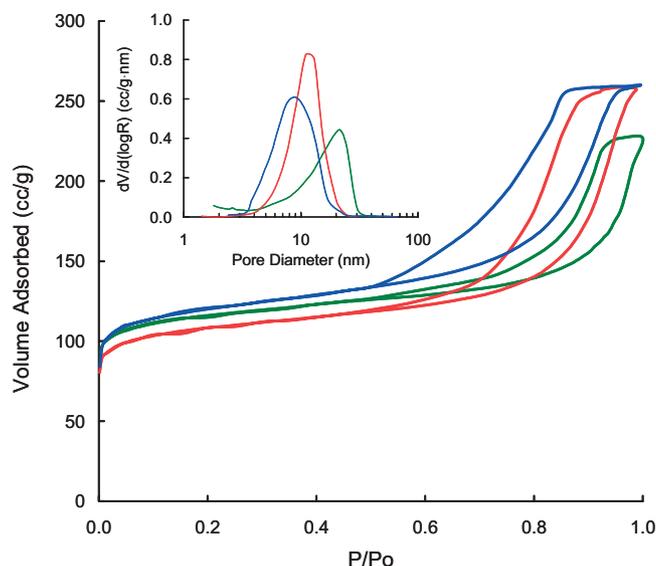
and surfactant, as evidenced by the gradual disappearance of the XRD peaks. This likely caused the lamellar structure to reorganize into surfactant-rich regions surrounded by hydrophobic polyfurfuryl chains, giving rise to the foam-like precursor of the final CNF material.

Carbonization of the cured sample was performed at 800 °C in an inert atmosphere, and the resulting nanostructured carbon displayed a foam-like microstructure with a 3D network of pores (see Fig. 2a) and thick (15–25 nm) semicrystalline pore walls with a d spacing of ~ 0.3 nm (Fig. 2b). While the fast Fourier-transform (FFT) image (Fig. 2b, inset) clearly illustrated the local crystallinity of CNF, no sharp diffraction peaks were observed in the XRD pattern, suggesting that the crystalline domains within the CNF material were small (~ 5–10 nm). It should be noted, however, that in the absence of surfactant, the synthesis gave rise to a glassy carbon material containing no crystalline domains, suggesting that the surfactant played a role in creating the small crystalline carbon domains. This effect was also observed when furfuryl alcohol was templated by a layered clay.[14,15] Therefore, CNF is a novel nanoporous carbon material that contains both porosity and small-scale crystallinity due to its surfactant-templated synthesis.

CNF possessed a BET surface area of ~ 400 m² g⁻¹ and a total pore volume of ~ 0.4 cm³ g⁻¹ (see SI Table S2). This is lower than observed for mesoporous carbons prepared using mesoporous silica as a mold.[10–16] However, our surfactant-templated carbon has remarkably thick pore walls that significantly increased its mechanical stability and allowed for the presence of nanometer-sized crystalline domains. Both microporosity (~ 0.15 cm³ g⁻¹) and mesoporosity (~ 0.25 cm³ g⁻¹) were found in CNF. This self-assembled carbon material exhibited a fairly narrow mesopore size distribution (see Fig. 3). Unlike previous study,[21] in the case of CNF, the surfactant dimension determined the initial lamellar structure, which then gave rise to a foam-like material with a median mesopore size that varied with the surfactant chain length (see Fig. 3). The mesostructure of CNF was remarkably stable, unlike that of the ordered mesoporous carbon material prepared with Pluronic© and resorcinol-formaldehyde, which lost its meso-
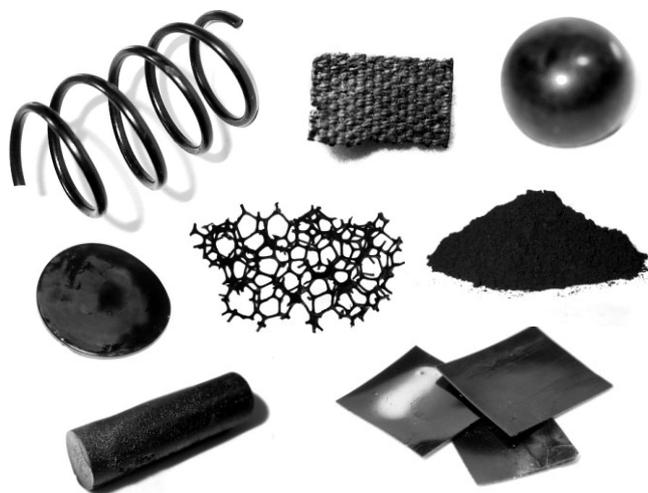

Figure 3. Nitrogen adsorption-desorption isotherms (Micromeritics ASAP 2010) and BJH desorption mesopore size distributions (inset) of CNF materials prepared under the same synthesis conditions with hexadecanol (—), octadecanol (—) and docosanol (—) as the surfactants. A weight ratio of 1:1 was used for the furfuryl alcohol-surfactant mixtures.

porosity at 700 °C.[20] CNF did not show any noticeable loss in mesoporosity even after heating in nitrogen at 1200 °C for 8 h (see SI Fig. S1). In contrast, significant reduction in microporosity (from ~ 0.15 cm³ g⁻¹ to ~ 0.08 cm³ g⁻¹) was observed, most probably due to a greater ordering of the carbon's long-range structure.

CNF could be readily prepared in a wide variety of sizes, shapes and forms without the need for solvents or binders (see Fig. 4), as its liquid-phase precursors could be poured into different molds for curing. The viscous precursor could also be coated onto various substrates, such as cloths, felts and papers, which would be removed during carbonization, yielding bulk monoliths of CNF containing the macroscopic features of the original substrate's void spaces.

In the synthesis of fine chemicals and pharmaceuticals, catalysts with high activity and long lifetime are pivotal to the economic operation of chemical processes. For supported metal catalysts, these characteristics are challenged by the tendency of metal nanoparticles to agglomerate and sinter.[22] For example, Heck reaction, which is one of the most powerful carbon-carbon coupling reactions in organic chemistry, is limited by catalysts that have low oxygen tolerance and poor reusability.[23–25] CNF was examined as a novel Heck catalyst support for vapor-grafted palladium clusters. The vapor grafting procedure involved an organopalladium complex as described elsewhere,[26,27] and readily produced palladium nanoclusters of 2–3 nm (see Fig. 5a) within the mesopores of the

Figure 2. a) High-resolution transmission electron micrograph (HR-TEM) of a microtomed CNF sample illustrating the network of interconnected nanopores (JEOL 2010 microscope, 200 kV). b) HR-TEM and FFT image (inset) of the CNF framework, illustrating the semicrystallinity of the pore walls, which have a d spacing (~ 0.3 nm) similar to graphite.

Figure 4. CNF prepared in a wide variety of shapes and forms: coils, cloths, spheres, discs, foams, powders, rods, and thin films.

CNF support. The resulting Pd/CNF catalyst contained 5.3 wt % Pd, and its performance was compared with a commercially available catalyst, 5 wt % Pd supported on activated carbon (Pd/C-1).

The catalysts were tested for the Heck coupling of 4-bromoacetophenone and n-butyl acrylate at 140 °C in argon. Pd/C-1 and Pd/CNF showed high turnover frequencies (TOF) of 3270 h^{-1} and 2480 h^{-1}, respectively. After reaching full conversion in the first run with a good total turnover number (TON) of 3700 (mole of product)/(mole of Pd), new reagents were added to the catalyst-containing reaction medium that had been maintained at 140 °C in argon for 24 h, and the reaction was initiated a second time. Negligible activity was observed with Pd/C-1 in the second run (TOF < 1 h^{-1}) even after 24 h, which was consistent with previous reports.[28] In contrast, Pd/CNF demonstrated a remarkable

Figure 5. a) TEM of Pd/CNF following vapor grafting of organopalladium complex at 80 °C. Palladium clusters of 2–3 nm were shown to be highly dispersed within the CNF support. (Inset) HR-TEM of a representative Pd nanocrystallite, illustrating its crystallinity, the typical d spacing of Pd, and a highly faceted crystallite morphology. b) TEM of Pd/CNF after three Heck reaction runs at 140 °C in air (with a total TON of 11,100). The Pd nanocrystallites remained ~ 3 nm in diameter after the reactions.
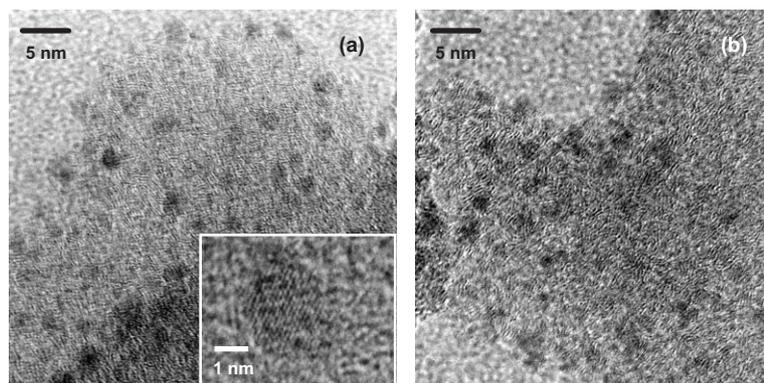
TOF of 2890 h^{-1} in its second run, which was greater than the TOF in its first run.

The catalysts were also evaluated for reusability in air; they were placed within a "filter membrane" that was recovered from the flask at the conclusion of each run. The Pd/C-1 catalyst showed good activity for its first run in air, but exhibited no activity upon reuse. In contrast, the Pd/CNF catalyst was fully recyclable after three runs in air, achieving a total TON of 11,100.

Most conventional Heck catalysts would show significant Pd cluster agglomeration and growth after just one reaction run.[29] In contrast, Pd/CNF exhibited negligible palladium cluster growth even after three runs at 140 °C (see Fig. 5b); the mean palladium cluster size was kept at ~ 3 nm, and the particles remained highly dispersed within the mesoporous framework of CNF even after exposure to air during reactions. This is a significant finding since heterogeneous palladium Heck catalyst systems, including Pd/C, usually show considerable palladium cluster growth after reaction.[23] Consequently, little catalytic activity was achieved by the recycled Pd/C catalyst.[28] In contrast, Pd/CNF was able to retain its catalytic activity over multiple cycles; this could be attributed to its stability against palladium cluster growth.

X-ray photoelectron spectroscopy (XPS) showed that nearly all of the surface palladium species in Pd/CNF were Pd^0 before and after three runs in air (see SI Fig. S2e and f, respectively). This supported the finding that no hydrogen reduction was needed to regenerate Pd/CNF between runs, unlike many oxide-supported Heck catalysts. The lack of palladium oxidation might be due to a strong interaction between the palladium cluster and the CNF support. However, no significant binding energy shifts were observed in the XPS peaks that could be indicative of a Pd-CNF electronic interaction. Raman spectroscopy also showed no significant shifts in the CNF peaks after Pd vapor grafting. Pd/CNF was further examined to see if the Pd clusters had adopted a quasi-2D morphology on the surface of CNF, in which case one would expect the normally diamagnetic Pd species to become paramagnetic.[29–31] SQUID measurements on Pd/CNF at 4 K showed no significant paramagnetic or ferromagnetic moments, suggesting that either the palladium loading was insufficient to generate a signal, or the palladium clusters, while small and faceted (see Fig. 5a), were not fine enough to adopt a quasi-2D structure on CNF surface.

The as-received Pd/C-1 catalyst contained mainly Pd^{2+} species (SI Fig. S2a), most likely in the form of palladium oxide (PdO).[32] XPS also showed that most of the palladium species were lost after one run, indicating that the palladium species were leached from the activated carbon surface rapidly during reaction. The results suggested that the Pd^{2+} species leached more readily from the support than the Pd^0 species. Since the Pd^0 species were stabilized in Pd/CNF, palladium

leaching was minimized, and significant catalytic reactivity was retained by this system over the course of several reaction runs.

Palladium (9.0 wt %) was also vapor-grafted onto Darco activated carbon after degassing the support at 180 °C *in vacuo* for 24 h. The resulting Pd/C-2 catalyst was then placed in a filter membrane and tested at 140 °C in air. It showed TOF's of 730, 160, and 4 h^{-1} in its first, second and third runs, respectively. Compared to the commercially available Pd/C-1 catalyst, Pd/C-2 showed somewhat better reusability, but still suffered from significant deactivation by its third run with < 6 % conversion after 24 h.

TEM showed that the as-prepared Pd/C-2 catalyst consisted of palladium clusters of 3–5 nm (see SI Fig. S3a), and the palladium dispersion on activated carbon was not as high as that on CNF, possibly due to the pore structure differences in the two supports. TEM and XPS revealed that significant amount of the palladium clusters had leached out from Pd/C-2 over three runs (see SI Figs. S3b and S2d). The remaining palladium clusters had grown to 10–20 nm (see SI Fig. S3b). Thus, although Pd/C-2 was obtained by organopalladium vapor grafting in the same manner as Pd/CNF, it suffered from significant deactivation due to Pd leaching and agglomeration. This study illustrated that it was important not only to obtain highly dispersed palladium clusters by vapor grafting, but also to use an appropriate support to stabilize palladium against leaching and cluster growth. Thus, the mesoporosity and semicrystalline walls of CNF were important factors towards preventing palladium oxidation, agglomeration and leaching, allowing a robust and reusable Pd/CNF catalyst to be achieved for Heck coupling.

The mechanism of Heck catalysis remains controversial as to whether the reaction is catalyzed by heterogeneous palladium clusters or by palladium species that leach into solution.[33–35] The following test was conducted to investigate if active soluble species were present in our reaction solution. After two runs of complete conversion over Pd/CNF at 140 °C under argon, the hot reaction solution was separated from the filtered catalyst under argon and allowed to cool. Fresh 4-bromoacetophenone, sodium acetate and *n*-butyl acrylate reagents were then added to the reacted solution, which was reheated to 140 °C under argon for further reaction. No conversion of the fresh reagents was observed after 24 h, indicating that soluble Pd species, while likely present in the reaction solution, were not active for the Heck reaction under these conditions. This study suggested that the CNF supported Pd^0 clusters were responsible for the catalytic activity.

In summary, a new surfactant-templated carbon material with tunable mesoporosity, CNF, was synthesized and applied as a support for palladium in the Heck reaction. The unique combination of semicrystalline and conductive framework, high surface area and interconnected porous structure allowed for the spontaneous reduction of a volatile Pd(II) complex within the CNF pores upon vapor grafting, and provided for the stabilization of highly dispersed Pd clusters over multiple reaction cycles. Pd/CNF successfully avoided Pd cluster

growth and agglomeration, and exhibited high activity even after multiple runs. These attractive properties of Pd/CNF may be extended to other Pd-catalyzed reactions. The stable Pd dispersion and oxidation state on CNF may also be attained for other transition metals supported on CNF for a variety of applications.

Experimental

Synthesis of CNF: In a typical synthesis, 5 g of hexadecanol and 5 g of furfuryl alcohol were mixed and slowly heated until a clear yellow solution was obtained; 0.15 g of *p*-toluene sulfonic acid solution (60 % w/w in water) was then added. (If a particular macroscopic shape was required, the CNF precursor solution would be transferred at this point to the desired mold for further processing.) The solution was kept at 40–50 °C to avoid solidification and to accelerate the polymerization of furfuryl alcohol. It would change from yellow to dark green to brown during the reaction. The temperature was then ramped to 80 °C under stirring to avoid solidification, and then to 100 °C and 120 °C for curing, after which the material could be ground down to a powder if desired. The final material was heated in N_2 at 800 °C for 5 h, or at a higher temperature if a higher degree of carbonization was needed.

Heck Reaction Studies: In a typical Heck reaction, 4.575 g (22.9 mmol) of 4-bromoacetophenone, 4.844 g (35.5 mmol) of sodium acetate trihydrate, 179 mL of dimethylacetamide, and 0.45 mL of dodecane (a chromatography internal standard) were introduced to a 250-mL Schlenk flask.

In an oxygen-free experiment, the flask would be subjected to 3 freeze-pump-thaw cycles to remove oxygen from the reagents and solvent, prior to catalyst addition in an argon-filled glove box. The sealed flask would then be connected to an argon line for reaction. For experiments performed in air, the flask would not be subjected to freeze-pump-thaw cycles, and the catalyst would not be introduced in a glove box. The amount of catalyst added (typically ~ 0.013 g) was based on the palladium content of the fresh catalyst, and was adjusted to give a TON of 3700 for each run with 100 % conversion.

After heating the reaction flask to 140 °C, the catalytic testing was initiated by adding an excess of *n*-butyl acrylate (4.04 mL, 28.1 mmol). Catalyst conversion was monitored via gas chromatography (Hewlett-Packard Model 5890).

Heck Catalyst Recycling Procedure: To facilitate catalyst recovery and reuse, catalyst powders were placed within an apparatus that was constructed out of a 0.7-μm glass fiber filter paper, with an outer cover made of 5-μm hydrophobic Teflon filter paper. This "filter membrane" was sealed with Teflon tape, and was introduced to the reaction flask. At the end of each run, the filter membrane would be removed from the flask in air, and washed with excess fresh dimethylacetamide and deionized water to remove residual chemicals from the catalyst surface. It was dried briefly in air at room temperature, and then introduced to a flask containing fresh solvent and reagents for the next run.

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