Selective and Efficient Impregnation of Metal Nanoparticles on Cup-Stacked-Type Carbon Nanofibers

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ABSTRACT

We describe the efficient impregnation of Pt nanoparticles (OD < 3 nm) on cup-stacked-type carbon nanofibers. The method involves the dispersion of the fibers in H_2PtCl_6 followed by low-temperature annealing. The Pt particle deposition is always homogeneous and can be controlled selectively on the outer or internal core using the hydrophobic nature of the material. Since the Pt particle activity on the fibers is high, this material could find applications as efficient catalysts and allied biological devices.

For a decade, nanocarbon materials have been widely studied as catalyst supports in heterogeneous catalysis because of their unique morphology and reactivity.[1–5] It is well known that the basic properties of impregnated catalysts are strongly affected by the impregnation method, the microstructure, the surface reactivity, and the metal precursor.[6,7] Among these factors, the morphology and nanostructure of supports are considered to be the main factors in obtaining high dispersions of nanoparticle catalysts. Here we demonstrate the selective impregnation of Pt nanoparticles in the hollow core and/or on the outer carbon nanofibers.

From the morphological viewpoint, conventional carbon nanotubes are made up of multiseamless nanosized cylinders of hexagonal carbon networks, which are not reactive.[8] Recently, a novel type of carbon nanofiber exhibiting cup-stacked morphology was developed as a novel and functional "tubular" nanosized material.[9] The main features of these morphologies consist of truncated conical graphene layers (cups) (see Figure 1) that exhibit a large central hollow core, which in turn imposes a large portion of exposed and reactive edges in both its outer surface and in the inner channel created within the carbon nanofibers. The utilization of these edge sites on the outer and inner surfaces and also the large-
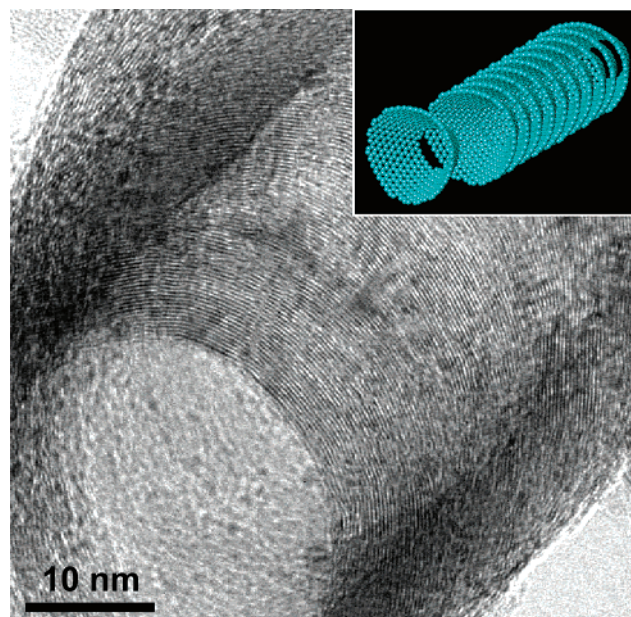
Figure 1. HRTEM images of a milled cup-stacked-type of carbon nanofiber at a tilted angle. The inset shows a schematic structural model.

scale and low-cost production of these nanofibers[10] make them excellent candidates for use as absorbent materials, catalyst supports, field emitters, and nanocomposites. Ap-

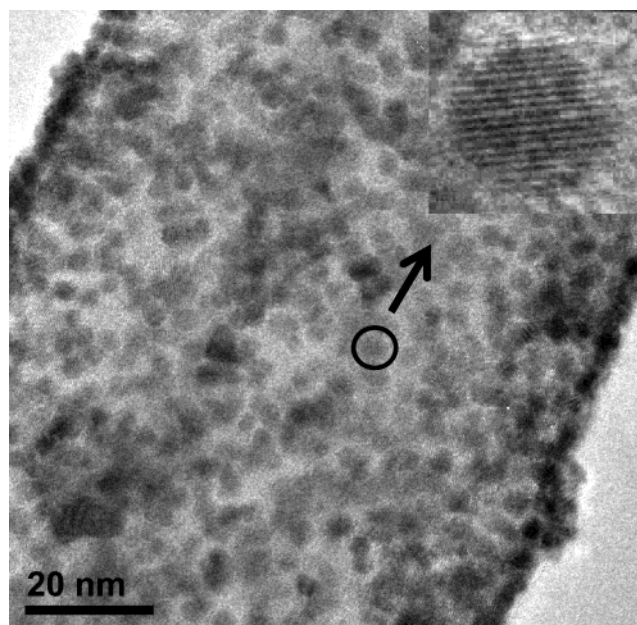* Corresponding author. E-mail: endo@endomoribu.shinshu-u.ac.jp.
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Figure 2. HRTEM image exhibiting a high dispersion of Pt nanoparticles only on the outer surface of a pristine nanofibers. The inset shows an enlarged view of an individual Pt cluster ($d_{(111)}$ = 2.26 Å).

plications of this novel type of carbon nanofiber as a catalyst support are also demonstrated here.

Three types of carbon nanofibers are used to induce selective impregnation of Pt nanoparticles in the outer surface or in the inner channel of nanofibers: pristine nanofibers,[9] shortened carbon nanofibers,[11] and duplex-type nanofibers.[9] The pristine nanofibers exhibit a relatively long and straight morphology with an entirely hollow open channel, exhibiting a diameter distribution ranging from 50 to 150 nm and lengths of up to 200 μm (specific surface area = 49.8 m^2/g).[9] To improve the diffusion rate of the Pt salt precursor both on the outer surface and in the hollow channel of the carbon nanofibers, the sample is ground through a ball-milling process, yielding a material with a specific surface area of 101.7 m^2/g. It is noteworthy that a higher reaction temperature in the synthesis of this carbon nanofibers induces the deposition of a pyrolytic carbon layer (duplex structure), resulting in a deactivation of the edge sites on the outer surface of the nanofibers. Pt dispersion on these three types of nanofibers is carried out via solution impregnation[6] and a reduction process as follows:[1] dispersion of nanofibers in distilled water using an ultrasonic process,[2] addition of an appropriate concentration (5−50 wt %) of hexacholoroplatinic acid (H$_2$PtCl$_6$) to the aqueous suspensions containing the nanofibers, followed by heating to 90 °C using the hotplate so that the solvent is completely evaporated during stirring,[3] and reduction to Pt nanoparticles at 300 °C in a hydrogen atmosphere (100 cm^3) for 3 h.
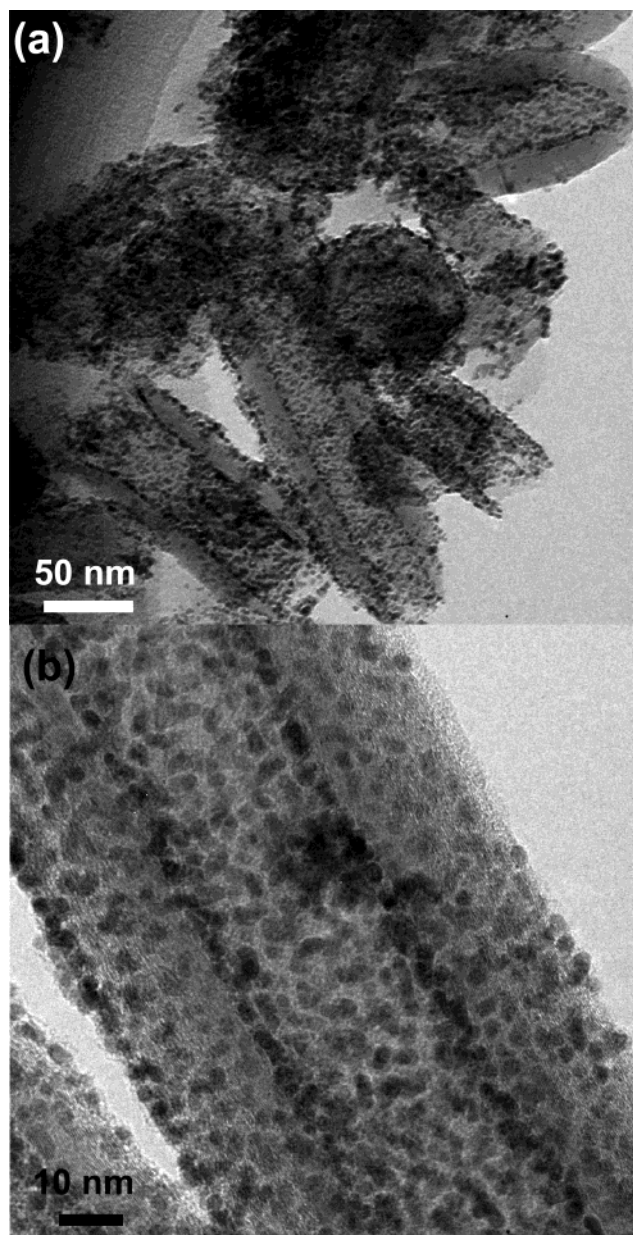
Selective impregnation only on the outer surface of the nanofibers is carried out using the pristine nanofibers. Utilizing the highly hydrophobic nature of carbon materials,[3] benzene was incorporated after adding a metal salt precursor. The addition of benzene during the process (described above) results in the impregnation of Pt nanoparticles only on the
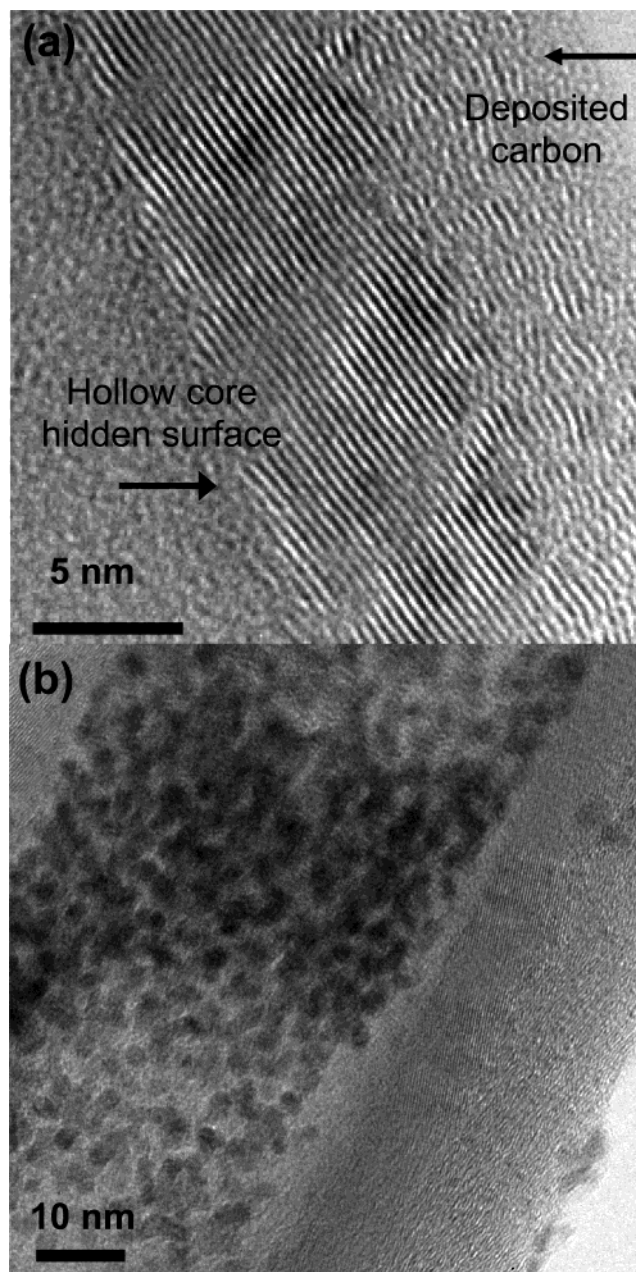
Figure 3. (a) TEM image of a duplex-type nanofiber and (b) dispersion of Pt nanoparticles only in the inner surface of the hollow core.

outer surface of the nanofibers after evaporation. A high-resolution TEM (HRTEM) image (Figure 2) shows homogeneously dispersed Pt nanoparticles (o.d. ca. 0.3 nm) appearing only on the outer surface. A closer observation of the Pt nanoparticles on the outer surface of the nanofibers indicates that they are crystalline with visible lattice fringes, which are identified as nanometer-sized single crystals with well-developed (111) planes. (See the inset in Figure 2.) For nanofibers containing a duplex structure (Figure 3a),[9] Pt nanocrystals are impregnated only in the inner hollow channel (Figure 3 b) because of the low reactivity of the edge sites through the deposition of pyrolytic (amorphous-like) carbon layers.[9] We believe that the activity in the inner channel is higher because the caps are truncated and therefore

Figure 5. Schematic model of Pt-particle-decorated cup-stacked carbon nanofibers due to a strong interaction between the metal salt and the edge planes.
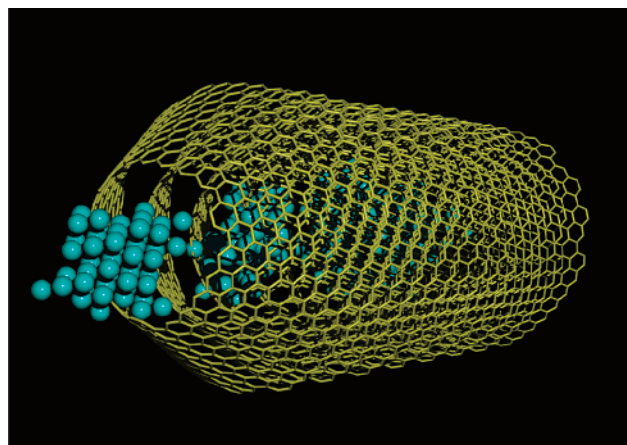
Figure 4. HRTEM image of highly dispersed Pt nanoparticles both on the outer surfaces and in the inner surfaces of the shortened nanofibers.

are more reactive because of the presence of carbon dangling bonds and strained curvature. Shortened nanofibers with two open ends induce a high diffusion rate and wetting of the metal salt precursor both on the outer and inner surfaces of the nanofibers (within a relatively short time), thus resulting in a homogeneous formation of Pt nanocrystals both on the exposed outer and "hidden" inner surfaces (Figure 4).

These experimental results indicate that the efficient deposition of Pt nanocrystals is due to a strong interaction between the metal salt precursor and the graphene edges (open) of the cup-stacked nanofibers. (See Figure 5.) Chemical functional groups (e.g., −COOH, −OH) derived from chemical oxidation processes are known to act as anchoring sites for metal nanoparticles;[3] unfortunately, these −COOH sites induce the impregnation of small and large

metal particles (broad distribution). Simply speaking, for oxidized nanofibers at 530 °C for 1 h in air, the diameter of metal particles deposited on the surface ranges from 2 to 20 nm (average = 7 nm). Therefore, we believe that the exposed edges (terminated as hydrogen−carbon bonds) are responsible for the selective anchoring of clusters of similar dimensions and result in a reduced tendency toward aggregation of the metal during the reduction process.

We have demonstrated that by tailoring the nanostructure morphology and the chemical reactivity of the nanofiber surface it is possible to impregnate metal nanoparticles homogeneously and selectively (up to 50 wt %) in the outer and inner "hidden" surfaces of cup-stacked nanofibers. We expect that other types of metal nanoparticles can be impregnated on this type of carbon nanofiber selectively using similar techniques.

The novel nanofibers impregnated with Pt nanoparticles offer the following advantages:[1] excellent dispersion of Pt nanoparticles (o.d. ca. 3 nm);[2] selective impregnation of Pt nanoparticles on the outer surface and/or inner surface;[3] and high potential as efficient catalysts in fuel cells. Other types of metals (e.g., Ag, Pd, Au, etc.) may be impregnated selectively or homogeneously on cup-stacked-type carbon nanofibers using the simple impregnation method (in progress). These decorated materials will certainly find applications in biological fields as drug carriers. However, this is the tip of the iceberg because additional applications of these novel cup-stacked nanofibers will probably emerge very shortly.

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