Facile fabrication of composites of platinum nanoparticles and amorphous carbon films by catalyzed carbonization of cellulose fibers

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Composites of platinum nanoparticles and amorphous carbon films have been facilely fabricated by catalyzed carbonization of cellulose fibers.

Metal nanoparticles are known to have unique features such as surface plasmon absorption and enhanced catalytic activity due to their quantum size confinements and extremely large surface areas.[1–3] Extensive studies have been carried out on the synthesis of colloidal metal nanoparticles stabilized by thiol compounds, polymers and surfactants in efforts to control their composition, size and shape, and to explore potential applications. Recently, direct synthesis of nanoparticles stabilized in solid matrices has been attracting increasing interests in terms of practical applications and synthetic challenges. For example, multilayered polymer films[4] and block copolymer films[5] were used as nanoreactors for formation of silver nanoparticles. Noble metal nanoparticles were synthesized in mesoporous silica films[6] and in ultrathin nanoporous TiO$_2$ films.[7] Silver particles of narrow size distribution were produced upon reversible redox transformation between metallic and oxide states in the latter matrix[8] and by grafting hydrophobic groups at the pore surface of mesoporous silica.[9] More complex nanostructures such as Ag-core/Pd-shell bimetallic nanoparticles were also fabricated *in situ* in nanoporous titania films, and the bimetallic particles exhibited an outstanding catalytic activity for hydrogenation of C=C bonds, as compared with those of Pd monometallic nanoparticles and Pd black.[10] Among these solid matrices, carbon-based materials including amorphous and graphitic carbons are particularly interesting and important. For example, carbon-supported Pt nanoparticles were prepared and tested as catalysts for fuel cells.[11] Amorphous carbon-activated palladium nanoparticles were synthesized by sonochemical decomposition of an organometallic precursor and showed catalytic activity in the Heck reaction.[12] Carbon-coated, ferromagnetic Fe, Co and Ni nanoparticles were prepared by a modified arc discharge process,[13] and silver nanoparticles encapsulated in carbon cages were reported by co-sputtering of the metal and graphite.[14] Bimetallic alloy nanoparticles were electrodeposited on an amorphous carbon electrode.[15] In this communication, we report a novel approach towards facile preparation of amorphous carbon fibers with immobilized Pt nanoparticles.

As shown by us recently, noble metal ions are effectively anchored on cellulose matrix, and are reduced to stable metal nanoparticles.[16] Adopting this procedure, a piece of lint-free cellulose paper (PS-2, Bemcot, 100% cellulose, Asahi Kasei, Japan) was used as the starting matrix. Platinum nanoparticles with a mean diameter of 5.7 nm and a standard deviation of 2.2 nm were produced in the cellulose matrix. The Pt/cellulose composite was then placed in a quartz tube furnace purged with nitrogen gas at 200 mL min^{-1}, and was carbonized at 400 °C for 30 min, and allowed to cool to room temperature. For comparison, a piece of the pure cellulose paper was also carbonized under otherwise identical conditions.

A much shrunk, deformed carbon residue was formed with a carbon yield of only *ca.* 5%, when pure cellulose paper was carbonized. Most of the cellulose mass was lost in to the N$_2$ flow. In contrast, a carbon yield of *ca.* 30 wt% was achieved from the Pt/cellulose composite. The carbon specimen was shrunk to a much

lesser extent, and almost kept its original shape. This higher carbon yield might be attributed to the catalytic effect of Pt nanoparticles which effectively dehydrate cellulose without predominant formation of gaseous carbon compounds.

ATR-FTIR spectra of the Pt/cellulose composite before and after carbonization indicate formation of amorphous carbon fibers. Scanning electron microscopy (SEM)† reveals for carbonized pure cellulose fibers a 66% decrease in fiber width (Fig. 1(a)) and formation of closely packed carbon particles (*ca.* 100 nm in diameter) on the surface of the fibers (Fig. 1(a), inset). In contrast, a much smaller decrease in fiber width (*ca.* 26%) is observed for the carbon fibers derived from the Pt/cellulose composite (Fig. 1(b)), and the surface of the individual carbon fiber is smooth (Fig. 1(b), inset). It is clear that very different surface morphologies are produced upon carbonization, depending on the presence and absence of Pt nanoparticles.

The Pt-nanoparticle-containing carbon paper was cut into small pieces and transferred onto a SiO-coated copper grid. TEM observation was performed after drying under vacuum overnight.‡ Fig. 2(a) shows a typical carbon fiber that contains well-dispersed Pt nanoparticles, as seen better in a magnified image (Fig. 2(b)). The mean diameter and standard deviation of the nanoparticles were estimated to be $d = 3.7$ nm and $\sigma = 1.4$ nm, respectively. A selected area electron diffraction (SAED) pattern (Fig. 2(c)) as revealed by focusing an electron beam on the nanoparticles matches those ((111), (200), (220), (311), (222)) of cubic metallic platinum. On the other hand, when the electron beam was focused on a carbon area which does not contain Pt nanoparticles, a diffuse halo of amorphous carbon appeared. Compared with a TEM image of the as-prepared Pt/cellulose composite, we conclude that carbonization did not cause significant changes in the size, size distribution and crystal structure of the Pt nanoparticles. Apparently, the carbon matrix acted as an effective barrier against aggregation of Pt nanoparticles in the Pt-catalyzed carbonization process. The amorphous carbon fibers are mesoporous, as indicated by the arrows in Fig. 2(b). The mesopores range in size from 5 to 10 nm. This is not surprising, since carbonization usually results in porous carbon materials such as charcoal. The amorphous nature of the carbon fibers was further confirmed by X-ray photoelectron spectroscopy (XPS).§ Since carbonization was carried out in nitrogen atmosphere, Pt must still exist in its metallic state. Thus the XPS peaks of Pt at 74.5 eV (4f$_{5/2}$) and 71.2 eV (4f$_{7/2}$) can be used as a standard to correct the binding energy of carbon. The carbon binding energy thus corrected is 284.4 eV, in agreement with the
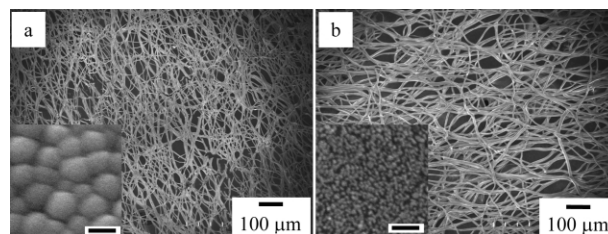

Fig. 1 SEM images of carbon fiber networks prepared by carbonization of pure cellulose (a) and Pt/cellulose composite (b). Insets are their individual fiber surfaces at a higher magnification: the scale bars are 100 nm.
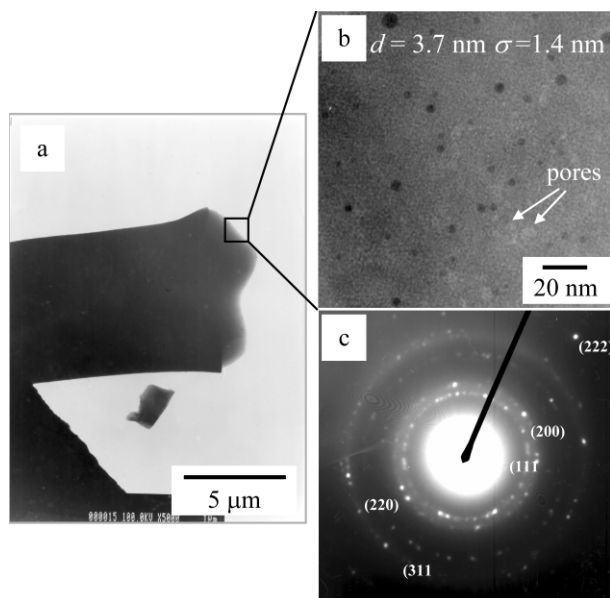
Fig. 2 (a) TEM image of carbon fibers prepared from a Pt/cellulose composite, (b) magnified image (the arrows point to pores), and (c) selected area electron diffraction pattern of the Pt nanoparticles.

known value of amorphous carbon (284.2–284.5 eV[17]). These XPS data give the composition of the Pt/carbon composite as 1 wt% of Pt and 99 wt% of C.

Cellulose microfibrils (10–30 nm) and their bundles are produced by mechanical disintegration, maceration, or chemical digestion. They are more suited for characterization of amorphous carbon nanofibers with immobilized metal nanoparticles. For this purpose, we used filter paper (Toyo Roshi Kaisha, Japan) as the carbon precursor. The filter paper is composed of broken fibers, the exposed strands including microfibrils and their bundles with diameters ranging from 10–30 nm up to several micrometers. Pt nanoparticles were synthesized in the filter paper,[16] which was then carbonized as described above with a yield of *ca*. 25%. The resulting carbon material retained the original shape of the filter paper. Fig. 3 shows typical TEM images of carbon nanofibers with well-dispersed Pt nanoparticles. The nanofibers are *ca*. 50 nm (Fig. 3(a)) and *ca*. 200 nm (Fig. 3(b)) in width, respectively. Fig. 3(c) is a magnified image which shows spherical Pt nanoparticles imbedded in amorphous carbon. The mean diameter and standard deviation of Pt nanoparticles were estimated from these TEM images, as $d = 4.9$ nm and $\sigma = 1.6$ nm, respectively. These values are similar to those estimated for the carbonized Pt/cellulose composite (Fig. 2). Larger Pt nanoparticles (several tens to *ca*. 200 nm) were also observed on the surface of fibers of micrometer
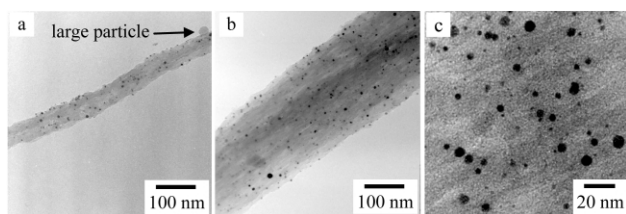

Fig. 3 Typical TEM images of Pt-nanoparticle-containing carbon nano-fibers obtained using filter paper as the carbon precursor: (a) *ca*. 50 nm in width, (b) *ca*. 200 nm in width, and (c) magnified image.

widths by SEM and TEM. The formation of such larger nanoparticles is apparently attributed to aggregation of smaller ones located on fiber surfaces. In contrast, only a few (Fig. 3(a), pointed by the arrow) or no (Fig. 3(b)) such particles were attached on the carbon nanofibers.

In summary, we have demonstrated a facile approach towards fabrication of amorphous carbon fibers with immobilized Pt nanoparticles. The implication of the current results are, at least, threefold. First, carbonization of cellulose is catalyzed by Pt nanoparticles and mesoporous amorphous carbon is obtainable in high yields. Second, most Pt nanoparticles are stable and remain unchanged in size during carbonization. This significant feature facilitates designed fabrication of various carbon-based functional materials with metal nanoparticles (*e.g.* catalysts). Finally, the facile, economical fabrication process allows for ready extension to the preparation of advanced nanocomposites, such as electrodes for fuel cells. Its practical potential is extensive.

Notes and references

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