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Fabrication of Ordered Uniform Porous Carbon Networks and Their Application to a Catalyst Supporter

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Uniform porous carbons have many useful applications in separation and electrode materials and have been reported through template approaches using zeolites or mesoporous hosts.[1,2] In this case, the porous carbons with uniform pore sizes of typically 0.2 to 5.0 nm were fabricated through carbonization of polymers templated by the inorganic porous hosts.[3] Colloidal crystalline templates based on spherical nanoparticles have been applied for the synthesis of much greater uniform meso- and macroporous materials, which include polymers,[4] inorganic oxides,[5] and metals.[6] Recently, this colloidal approach has been extended to the fabrication of new porous carbons. Uniform three-dimensional porous carbon replicas were made by CVD or plasma methods of methane or propylene as a feed gas against porous silica opals.[7] Mesoporous carbon was also reported using surfactant-stabilized silica particles prepared from an aqueous Ludox HS-40 silica sol.[8] However, pores were not distributed in an orderly fashion and not interconnected to each other. Recently, in our earlier work, the fabrication of new uniform porous carbons with air balls of 50−60 nm in diameter interconnected to each other was reported by carbonization of sugars and polymer.[9] The carbon capsules with hollow core/mesoporous shells were also synthesized using solid core/mesoporous shell silica spheres as templates.[10] Here we report the synthesis of uniform porous carbon replicas with interesting morphological variation against a colloidal crystal template by inducing different polymerization processes of phenol and formaldehyde as a carbon precursor. The processes of controlling the morphology in this work were simple and were well performed just by altering the acid catalyst sites, which control the initiation sites of the acid-catalyzed condensation reaction from the same precursor. In particular, these highly ordered uniform porous carbons resulted in much improved catalytic activity for methanol oxidation as a catalyst supporter in a fuel cell.

Several monodisperse silica nanoparticles in the range of 150−800 nm were prepared on the basis of a reported method.[11] Aluminum was incorporated into some of the silica particles through the impregnation method to generate strong acid catalyst sites.[12] Elemental analysis indicated a Si/Al mole ratio of about 14 for the resulting Al-implanted silica particles. The particles dispersed in water were then allowed to sink down slowly and were dried at 333 K in an oven after gently removing water above the silica deposit. Subsequently, the dried array of the silica spheres was sintered slightly at their points of contact to provide connectivity in resulting carbon replica by heating the array at about 1073 K for 2 h. Al-implanted silica particles themselves have strong acid sites on the surfaces, while pure silica particles needed sulfuric acid as an acid catalyst added externally to initiate the polymerization of phenol and formaldehyde. The mixture with molar composition of 1.0 phenol:0.8 formaldehyde:0.1 sulfuric acid prepared at 353 K under vigorous stirring was added into the void space of the colloidal silica template and then heated to 398 K for 12 h to obtain a cross-linked polymer. In the case of Al-implanted silicas, carbon precursor solution without sulfuric acid was added into the template array in the same way. Each of the composites prepared in two different ways was then carbonized by heating the composites at a slow increasing rate of 5 K/min to 1273 K in dry Ar flow. The resulting silica-carbon composites were subsequently etched off with 48% aqueous HF to dissolve the silica template, and resulting porous carbons were washed, filtered, and dried in an oven at 343 K. The two different processes resulted in interesting morphological alteration in the porous carbon network. The overall synthetic procedures are described in Scheme 1. A graphitic C−C stretching band at 1590 cm^{-1} increased, while the bands near 800−900 cm^{-1} due to C−H deformation and methylene cross-links on phenol rings decreased during carbonization in infrared spectra.[13]

Scheme 1

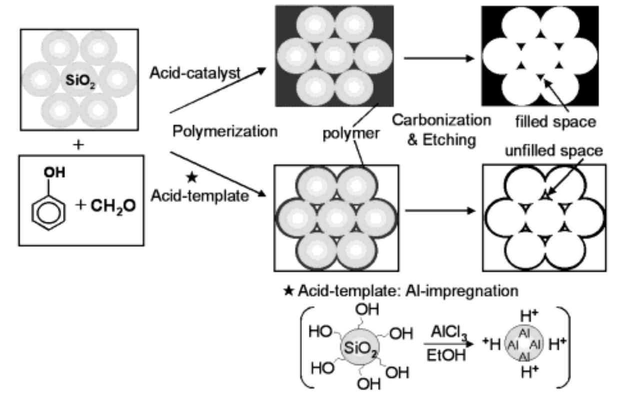

Figure 1 shows SEM images of the silica-carbon composites (insert) and the resulting silica-free carbon replicas with different morphologies. An Al-grafted silica array resulted in surface coating (surface templating) as shown in the silica-carbon composite and the corresponding carbon replica in Figure 1a. In this case, the polymerization was initiated on the particle surface by the acid catalyst sites on Al-implanted silica surface. The resulting hollow core carbon capsules with about 200 nm (about 20% shrinkage during replication from a 250 nm sphere) in diameter and 20 nm shell thickness were three-dimensionally interconnected through contact points appearing as small holes. However, when the acid catalyst is mixed with the precursor solution, the polymerization occurs everywhere to fill up the entire space between the particles. Figure 1b clearly shows the formation of ordered nanoporous carbon framework (volume templating) with complete filling of the entire void around the silica spheres. Each of the spherical pores is also interconnected through small holes. Similar volume and surface templated porous carbons were reported earlier.[7] However, the

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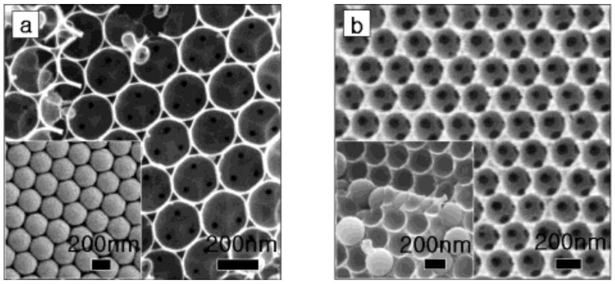

Figure 1. SEM images of carbon-colloidal silica composite (insert) and the corresponding silica-free carbon replica prepared (a) by surface templating and (b) by volume templating, using 250 nm silica spheres. Some of the silica spheres are seen in the composite in the insert of (b).

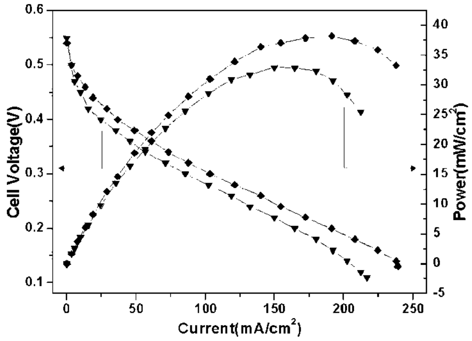

Figure 2. Comparison of the voltage and power density responses of the volume templated porous carbon-supported Pt(50)−Ru(50) alloy catalyst (−◆−) and the E-TEK counterpart (−▼−)in a direct methanol fuel cell. The DMFCs were operated at 303 K with the flow rate of 2 mL/min of 2 M CH_3OH at anode, 300 mL/min of O_2 gas at cathode, and Nafion 115 as electrolyte. Anode: 80 wt % porous carbon-supported Pt−Ru alloy catalyst (3.0 mg/cm^2) and 60 wt % E-TEK Pt−Ru alloy catalyst (4.1 mg/cm^2), respectively. Cathode: Johnson Matthey Pt black (5.6 mg/cm^2).

porous carbons were prepared from several different carbon precursors and carbonization processes.

High surface area and well-developed porosity are essential for a catalyst supporter to result in high catalytic activities. To investigate supporter effect, the Pt(50)−Ru(50) alloy catalysts were prepared by the borohydride reduction method[14] using our porous carbons and a carbon black called Vulcan XC-72[15] as a catalyst supporter. Homogeneous dispersion of Pt−Ru alloy metal particles with the size of about 2−3 nm over the carbons was detected in transmission electron microscope (TEM) images. This is further confirmed through average particle size analysis from a (220) X-ray diffraction peak of Pt fcc lattice by a Scherrer equation.[16] Cyclic voltammograms for methanol oxidation activities of Pt(50)−Ru(50) catalysts supported on the volume templated porous carbon and Vulcan XC-72 carbon, and of commercially available E-TEK Pt(50)−Ru(50) also supported on the Vulcan carbon, indicated that our volume templated carbon-supported catalyst outperformed the E-TEK one by about 30−40% and the Vulcan carbon-supported one by about 60%. This is really an amazing increase of the activity of the PtRu for the porous carbon versus the Vulcan carbon. Figure 2 shows the unit cell performance of the direct methanol fuel cell using the porous carbon-supported catalyst and the E-TEK catalyst. Our porous carbon-supported Pt−Ru alloy catalyst exhibited much higher specific activity for methanol oxidation than the E-TEK catalyst by about 15%.[17] BET surface areas of the porous carbon were determined to be 706 m^2/g (512 m^2/g and 194 m^2/g for micropores and macropores, respectively) and 139 m^2/g (34 m^2/g and 105 m^2/g for micropores and macropores, respectively) before and after the catalyst loading. BET surface areas of the Vulcan carbon and the E-TEK catalyst were found to be 216 m^2/g (84 m^2/g and 132 m^2/g for micropores and meso- or macropores, respectively) and 86 m^2/g (31 m^2/g and 55 m^2/g for micropores and meso- or macropores), respectively. The catalyst loading resulted in a drastic decrease in the surface areas. The catalysts may be mainly distributed in micropore areas as evidenced from the significant decrease of the micropores. The improved activity for the methanol oxidation is considered to be due to the higher surface area of the porous carbon for the catalyst dispersion, and also in part due to the three-dimensionally interconnected uniform macropores which favor efficient fuel and product diffusion in the porous carbon supporter as compared with the Vulcan carbons with randomly distributed pores of varying sizes which may make fuel and product diffusion difficult. Porous carbon with partially isolated pores with no interconnection gave poor catalytic activity, supporting the implication of pore connectivity.

The colloidal silica template presented in this work was a simple and viable route for production of uniform bulk macroporous carbons, whose pore sizes can be easily controlled by monitoring the sizes of silica spheres.[11,18] Thus, this method can cover an even smaller or larger range of pore sizes. The morphology of the resulting carbons was easily controlled by simply altering acid catalyst sites. In particular, the carbon with an interconnected uniform pore array demonstrated its possibility as a good catalyst supporter in a direct methanol fuel cell. Further work with different pore sizes as catalyst supporters is under progress.

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Supporting Information Available: CV activity data, TEM images, XRD patterns and chemical states (determined by XPS) of the PtRu, stability data, and TG analysis of the porous carbons and preparation methods for electrode and MEA (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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