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Fabrication of Mesoporous Carbon Tube and Foam: Application as Supports in Enantio-Selective Separation of Optically Pure Amino Acid from Racemates

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The mesoporous monolithic carbon (MMC) foams and carbon tubes were newly fabricated in cm-scale using the mixture of triblock copolymers and phenol/HCHO resin precursors. The regular mesoporosity were formed in the body of MMC foam and carbon fibers. In this work, the organic phases containing chiral ARCA adsorbent and a phase transfer catalyst were coated on the surfaces of mesoporous carbon support, and this ARCA/carbon mixture was adopted for the enantioselective separation of amino acid in the circulation system. (S)-ARCA coated MMC support showed high selcetivity up to 90% for the separation of *D*-type phenylalanine, serine and tryptophan from racemic mixtures.

Keywords: Mesoporous Carbon, Foam, Amino Acid, Chiral Separation, Adsorption.

1. INTRODUCTION

Mesoporous materials with a pore diameter in the range of 2∼10 nm may be suitable for a wide range of applications.[1,2] Formation of porosity on two or three different length scales with hierarchical structure may provide the easy diffusion of reactants to the active sites for catalysis and adsorption process. The synthesis of mesoporous composites by various procedures has been studied widely to develop the new catalysts.[3–6] Mesoporous silica, alumina and carbons are fundamental candidates for the use as a support. Among these materials, porous carbon has the big potential for practical uses.[7,8] In this study, we have fabricated the mesoporous monolithic carbon (MMC) foams and tubes. MMC foams in large size could be fabricated from the mixture of triblock copolymers and phenol/HCHO resin precursors. At the drying temperature higher than 300 °C, the sol precursors were expanded and solidified to make the MMC foams. As well the mesoporous carbon tubes were synthesized by coating of above sol on the surface of silica fibers.

After carbonization of carbon/silica composite at 900 °C and dissolution of silica by HF, large fractions of macroporosity in three dimensions were formed in the monolith body, and the remaining carbon walls exhibited uniform mesoporosity.

Optically pure D-amino acids (AA) are industrially important chiral building blocks for the synthesis of pharmaceuticals, food ingredients, and drug intermediates.[9–12] The syntheses of optically pure chemicals have gained significant potential over recent years. Chemoenzymatic dynamic kinetic-resolution processes have recently been developed for deracemization of amino acids.[13] (S)-ARCA (Alanine Racemase Chiral Analogue) is a good candidate for the selective adsorption of D-AA through imine formation reaction.[14] In this work, the organic phases containing (S)-ARCA adsorbent and Ionic Liquid (as a phase transfer catalyst; PTC) were coated on the surfaces of mesoporous carbon supports for selective separation of D-AA in the circulation system. The heterogeneous adsorbents were loaded in the continuous flow type packing bed. This heterogenized system has overcome the disadvantage of homogeneous liquid–liquid extraction process for

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the separation of D-AA using ARCA. (S)-ARCA coated on MMC support has a unique property for the selective adsorption of D-AA (up to 90% selcetivity) from racemic mixtures.

2. EXPERIMENTAL DETAILS

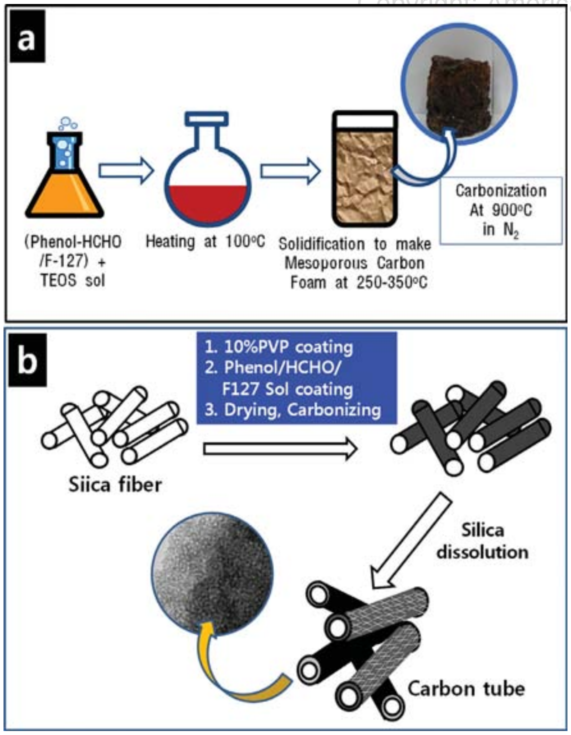
2.1. Materials Synthesis

The starting carbon sol and the low-molecular-weight phenolic resin/silica sol precursors were prepared according to the method reported previously in the papers.[15, 16] This carbon sol or carbon/silica composite sol was concentrated by evaporating the solvent, until the volume of sol mixture was reduced to 1/3 as compared to the starting volume. Then it was kept at 300 °C for self-expansion during the solidification of sol into gel foam. The typical procedure to fabricate the mesoporous carbon foam is shown in Scheme 1(a). The carbon precursor sol was coated on the surfaces of silica fibers modified by PVP and NH_4F. This carbon/silica composite was dried without washing, and carbonized at 900 °C in N_2 stream.

The procedure to prepare the mesoporous carbon tube is shown also in Scheme 1(b).

2.2. Separation of D-AA from Racemic AA

Organic solution of 10 g of (S)-ARCA, 1.4 eq. of Ionic Liquid, 20 ml of EDC solvent was mixed until ARCA was fully dissolved. This solution was impregnated on MMC support and then it was packed in the tubular type reactor. The aqueous solution of 2.0 eq. D/L-phenylalanine, 2.0 eq. NaOH and 1.8 eq. DIPA dissolved in 200 ml of distilled water was pumped and circulated through the reactor packed with (S)-ARCA/carbon support for adrsorption of D-AA. The adsorption analysis was performed for one hour, and after changing the circulating solution as 3 M-HCl, the hydrolysis and back-extraction of adsopted AA into the acidified water was performed for additional 1 h with circulation by pump.



Scheme 1. Procedure for the fabrication of MMC foam (a) and mesoporous carbon tubes (b).

3. RESULTS AND DISCUSSION

The centimeter-scale MMC foam could be fabricated by using the mixture of triblock copolymers and phenol/HCHO resin precursors basically. The optical and SEM, TEM images of MMCs are shown in Figure 1. For the fabrication of MMC foams, by incorporating TEOS sol in the carbon sol mixture, it was expanded more efficiently to make the foam structure. The size, density and bulk shape of MMC foam could be controlled, according to the container and treated heating temperatures (Figs. 1(a), (b)). The body volume of MMC foam was reduced after carbonization at 900 °C. Figure 1 also shows the shape of the carbonized MMC foam made by replicating the shape of container. It is clearly found that large fractions of macroporosity in three dimensions are observed on cross-sectional SEM images of MMC foam (Fig. 1(d)). The formation of mesopores in MMC foam walls could be confirmed by TEM (Fig. 1(e)) and BET analysis (Fig. 1(g)). This carbon showed high surface areas such as 1100 m^2/g and pore volume of 0.71 cm^3/g with mean pore size of 55 Å.

The mesopores were successfully incorporated inside the wall of carbon tubes by carbonization of phenol/HCHO/F127 carbon sols coated on the silica fibers after dissolution of silica by HF (shown in Scheme 1(b)). The analytical results by SEM, XRD and TEM revealed that the materials had well developed pore with a large specific area. Optical microscopic images (Fig. 2(A)) and SEM photographs (Fig. 2(b)) show the vacant inside of carbon tubes. The bundle type carbon tubes were easily obtained by coating of carbon sols (Fig. 2(c)).

TEM image of monolith sample (Fig. 2(d)) displays a hexagonal array of pore structure for the carbon tubes. However the mesoporosity was observed throughout the whole carbon tubes. N_2 adsorption–desorption isotherm of carbon tubes display steep changes with pressure, which is an indication of the presence of mesoporosity (Fig. 2(e)), showing surface area of 800 m^2/g and pore volume of 0.54 cm^3/g with mean pore size 50 Å. The wall thickness of carbon tubes was around 1 μm.

The racemic D/L-AA is consisting of 50% D-AA and 50% L-AA. (S)-ARCA forms an imine group with D-AA in major under the basic condition around pH 10. As a

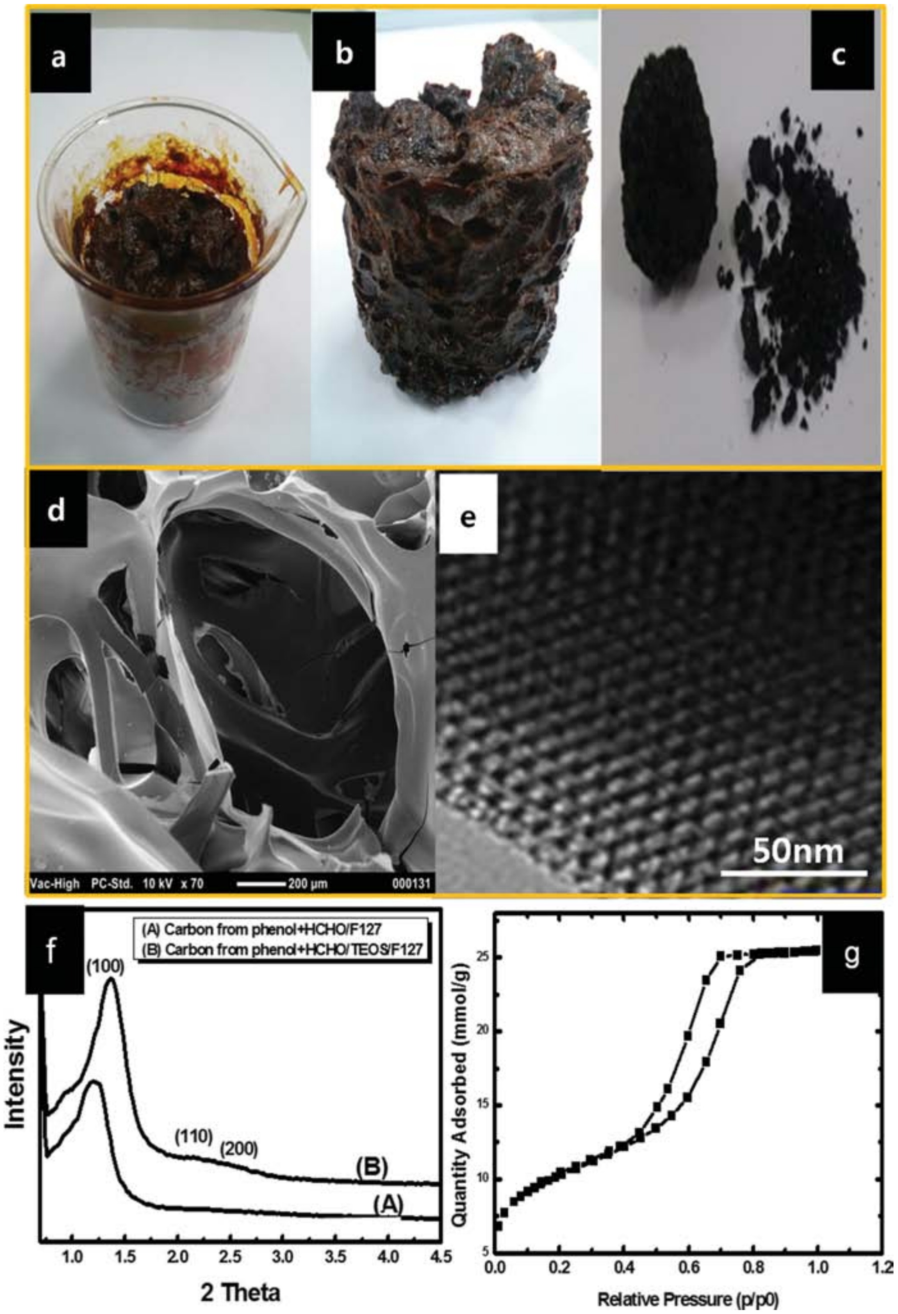


Figure 1. OM image of dried MMC in beaker (a), removal of container after polymerization (b), after carbonization (c). SEM (d) and TEM (e) image, XRD patterns (f) and N_2 adsorption–desorption isotherm (g) of MMC.

maximum, only 1.0 eq. (S)-ARCA in organic solvent reacts theoretically with 1.0 eq. D-AA from 2.0 eq. racemic D/L-AA, leaving 1.0 eq. of L-AA in the aqueous layer. High molecular weight chiral aldehyde compound such as ARCA is soluble only in organic solvent such as methylene chloride. The conventional adsorption is going on through liquid–liquid extraction process. Since AA is soluble in an aqueous phase as well ARCA is dissolved in the organic phase, PTC is absolutely needed for fast diffusion of AA into organic layer to contact with ARCA. This Adsorption/Desorption process is briefly summarized in Scheme 2. For the successful application in our work, ARCA, PTC and ionic liquid were dissolved in the organic solvent, and then the mixture was impregnated on the

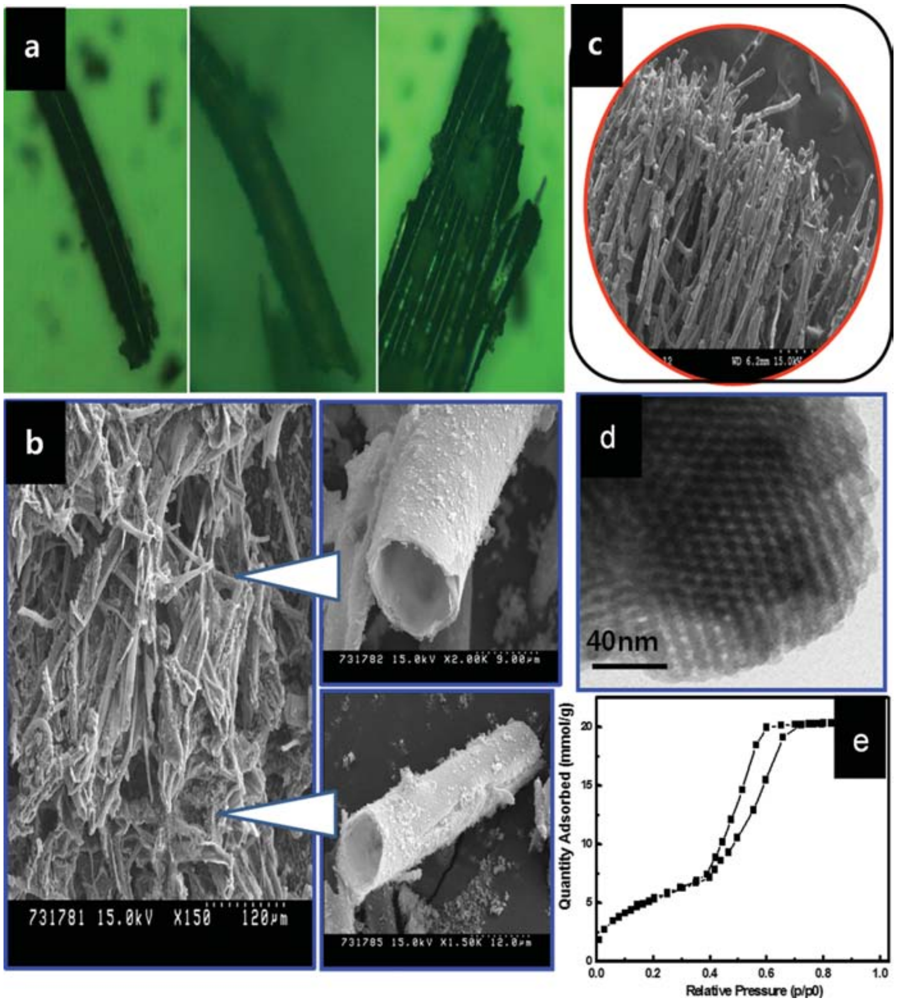
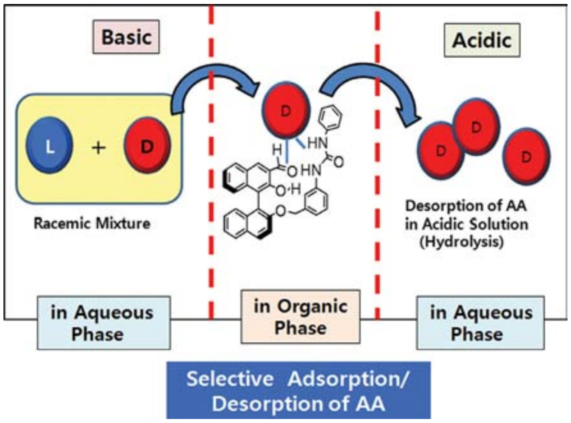


Figure 2. OM (a), SEM (b), (c) and TEM (d) images and N_2 adsorption–desorption isotherm (e) of mesoporous carbon tubes.

MMC foams or carbon tubes. The AA dissolved in basic water was efficiently contacted to ARCA on carbon support during the circulating process. At the high loading of new ionic liquid, a full dissolution and homogeneous coating of ARCA were achieved. In the heterogenized ARCA system, phase separation into organic layer and aqueous layer was unnecessary. Adsorpted D-AA was desorpted and released into the aqueous HCl solution from ARCA adsorbents coated on the carbon support through hydrolysis. To increase the adsorption rates, (S)-ARCA and PTC were coated on the carbon support as thin layers. The mesoporous support provided excellent property for homogeneous loading of chiral ARCA on the surfaces as thin layer. In the repeated adsorption, maximum adsorption of 95% D-amino acid was achieved in the batch and contineous circulation system. The high purity of D-AA up to 95% could be obtained by adsorptive separation in the continuous system.



Scheme 2. Selective adsorptive separation of chiral AA by ARCA.

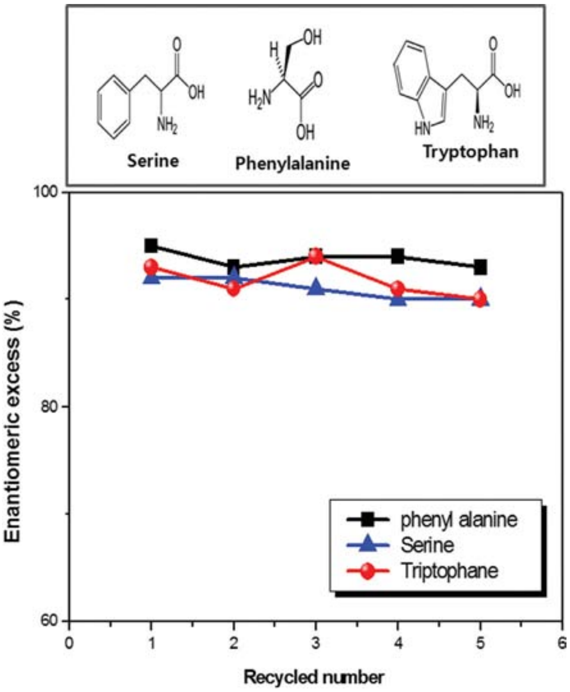


Figure 3. Enantiomeric excess % of produced AA in recycled reaction (flow rate; 200 ml/min in the fixed type reactor, MMC was used as a support).

Figure 3 shows that the heterogenized ARCA has adsorpted chiral D-AAs (Phenylalanine, Serine and Triptophan) enantioselectively for more than 5 times reuse without any purification.

4. CONCLUSION

The porous carbon foam and tube materials having bimodal pore structures were fabricated for anchoring the enantioselective chiral adsorbents. These carbon supports were used for the selective separation of D-AA from racemic AA in the continuous flow type packed bed reactor system. The unique separation properties in heterogenized adsorption system may expand the applications of porous materials for commercial processes in the future. Such carbon materials with bimodal meso/macroscopic pores would be useful for many potential applications, such as heterogeneous catalysts when bulky reactant molecules are involved.

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