

Electrophoretic assembly of nanozeolites: zeolite coated fibers and hollow zeolite fibers†

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Zeolite coated fibers with compact and full deposits have been fabricated by electrophoretic deposition of nanozeolites onto carbon fibers, whereafter hollow zeolite fibers have been obtained by calcination to remove the substrates.

Zeolites have been widely used in various fields as a class of crystalline materials with unique properties such as large microporosity, molecular sieving behavior and high hydrothermal stability. Construction of zeolite coated fibers and hollow zeolite fibers with designed structures has attracted considerable attention due to their fast diffusion and low pressure drop while maintaining high catalytic efficiency.^{1–3} Although several methods have been put forward to prepare these materials, such as *in situ* soft solution process,¹ *in situ* zeolite deposition² and seed film method,³ they all suffer from the drawback that the film thickness and the zeolite particle size are difficult to control. In addition, it is difficult for the last two methods to avoid the zeolites crystallizing concurrently in the synthesis solution. To overcome the limitations above, the layer-by-layer (LbL) technique has been utilized recently to prepare hollow zeolite fibers in our laboratory.⁴ The products prepared by LbL are expected to be more favorable for mass transfer due to their solely nanozeolite composed walls whose thickness is convenient to control.

Electrophoretic deposition (EPD) is another effective and controllable method to assemble charged colloid particles.^{5–13} The advantages of the EPD process are twofold: one is the fine uniformity of the deposition, the other is the easy manipulation and convenient control of the process.^{7,8} The performance of the EPD method has made it an attractive route to effectively manufacture ordered structures of colloidal systems, such as micrometer-sized silica colloids, polystyrene latexes,^{5,6,9,10} nanometer-sized gold colloids,^{7,11} and submicron ceramic powders.^{12,13} The EPD technique is also used to modify electrodes.^{14–16} A Pt disk electrode modified with a large crystal zeolite/polymer coating of *ca.* 11 micron thickness was obtained by the high-voltage (200 V) EPD technique in organic solution.^{15,16} Recently, nanozeolites have proved to be efficient ‘building blocks’ to construct hierarchical structures for their colloidal character and surface charge.^{4,17,18} Here, exploiting the characteristic properties of nanozeolites, the EPD technique has been used for the first time to fabricate zeolite coated carbon fibers (ZCFs) and hollow zeolite fibers (HZFs) with ultra-thin walls of nanozeolite under low voltage (1–3 V) in aqueous solution.

The preparation of ZCFs was operated in an electrophoretic cell, where a cathodic carbon fiber (*ca.* 7 μm diameter, 2 cm length) bundle was centered in a cylindrical platinum container (*ca.* 2.75 cm diameter) which served as the anode. In this arrangement, voltages were controlled by a CHI660 Electrochemical Workstation. Nanocrystals of silicalite-1 (95 \pm 10 nm diameter, determined by DLS) were prepared and purified by a

literature method.¹⁹ Suspensions for EPD experiments were obtained by dispersing the nanosilicalite-1 in distilled water to a concentration of *ca.* 1.5 wt%. The pH of the suspension was adjusted with 0.1 M HCl. Prior to use, the carbon fibers were cleaned according to the literature.³ To yield HZFs, ZCFs were heated to 873 K at a heating rate of 5 K min⁻¹ in nitrogen and kept for 4 h, then calcined in air for 8 h at the same temperature to remove the substrates.

Dense and complete deposition of nanozeolites on carbon fibers is an essential requirement for the preparation of perfect ZCFs as well as intact HZFs by the EPD technique. The success of deposition relies on conditioning two sequential steps (i) the motion of particles towards the electrode and (ii) the formation of a coherent deposit on the electrode surface by overcoming the electrostatic repulsion arising from the similar charge of nanoparticles.^{5,8} It has been suggested the latter step is induced by lateral interaction between the deposited particles caused by electrodynamic flows which result from distortions in the applied electric field and the passage of ionic current through the solution.^{5,6,20} The modulation of the entire process thereby can be fulfilled by changing the particle charge and the field strength. Hence, the pH of the suspension and the voltage exerted on the electrophoretic cell are important variables.

At pH 6 the zeta potential of the nanosilicalite-1 particles was only +4.5 mV (DELSA 440SX), thus zeolite particles prefer to coalesce and form aggregates in solution during the EPD process. When the pH was adjusted to 4.5, there were largely uncoated areas on the carbon substrates. This can be explained by the electrical force driving nanoparticles towards the cathode being too weak to form complete and dense deposits although the zeta potential rose to +21.1 mV. The best result was obtained at pH 2.5 [Fig. 1(b)]. All longitudinal strips on the original carbon fibers [Fig. 1(a)] disappeared, implying that the deposits obtained at pH 2.5 [Fig. 1(b)] were compact and complete due to the high zeta potential of +46.8 mV. This result illustrates

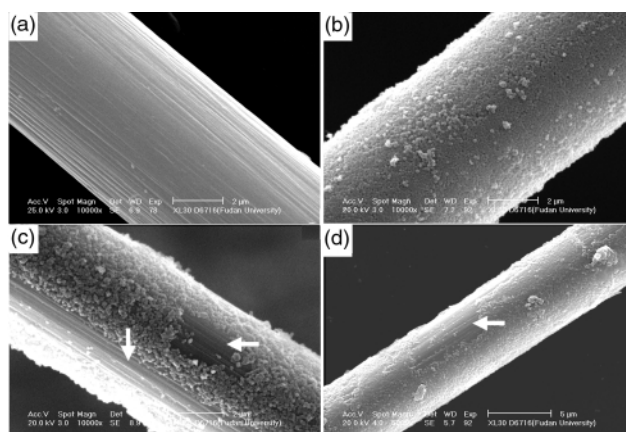


Fig. 1 SEM images of original carbon fibers (a) and zeolite coated fibers prepared under voltages of 2 V (b), 1 V (c) and 3 V (d) at pH 2.5 for 2 \times 10 min.

† Electronic supplementary information (ESI) available. XRD patterns and other related SEM images of zeolite coated fibers and hollow zeolite fibers. See <http://www.rsc.org/suppdata/cc/b0/b010197o/>

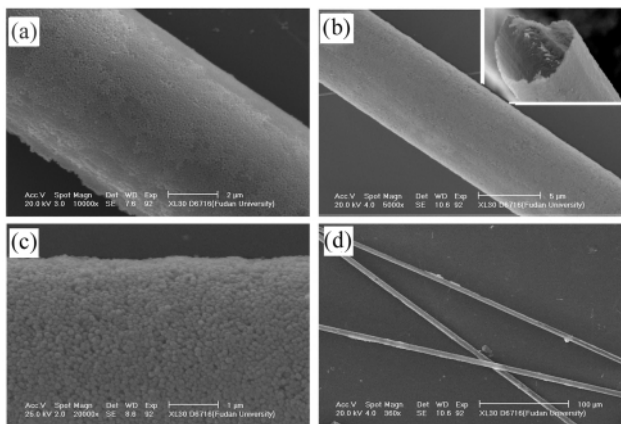


Fig. 2 SEM images of zeolite coated fibers (a) and hollow zeolite fibers (b, c, d) prepared at pH 2.5 and step voltage 1 V, 2×10 min; 2 V, 2×10 min; (c) and (d) are high and low magnification micrographs of (b), respectively.

how the particle mobility towards the cathode is largely enhanced as the zeta potential increases,⁹ thereby facilitating the formation of complete deposits on the cathode. Upon applying different voltages, such as 1, 2 and 3 V, each for two cycles of 10 min (2×10 min), the deposit thickness increased with increased voltage. There were many bare areas when applying 1 V [see arrows in Fig. 1(c)] due to insufficient particles being deposited on the cathode. In addition, it is noticeable that most of the particles on the fibers assembled in large or small clusters, implying the existence of lateral motion of the particles on the electrode.⁶ When 2 V was applied, the fibers were fully coated with nanozeolites as shown in Fig. 1(b), attributed to the improved rate of particle movement towards the cathode under increased electric field. At 3 V, although deposits on some areas of the fibers were thicker, some bare areas were found again [Fig. 1(d)]. The reason for this may be the production of hydrogen due to the electrolysis of water at the cathode which hinders the deposition or peels the deposited layer off the electrode.²¹ Water electrolysis was also established by the current vs. time curve at 3 V. Unlike the monotonously decreasing current with time at 2 V this exhibited an increasing trend as well as fluctuation at 3 V. The EPD process at 2 V provides a feasible route to fabricate ZCFs with compact and complete deposits under appropriate conditions.

To fabricate ZCFs with denser and thicker coatings and further obtain intact HZFs, two improved processes have been adopted: (i) lengthening the deposition time from 2 V, 2×10 min to 2 V, 2×20 min, (ii) the application of a step voltage: 1 V, 2×10 min; 2 V, 2×10 min. Although both procedures improved the quality of deposits and produced intact HZFs after removal of the carbon substrates, the walls of fibers prepared by the latter method were more smooth and uniform. Fig. 2(a) shows that ZCFs prepared *via* the step voltage possessed even and dense zeolite films instead of the original texture of the carbon fibers [Fig. 1(a)]. After calcination the carbon substrates in the ZCFs were removed and hollow fibers with uniform walls were obtained [Fig. 2(b) and inset]. A micrograph of HZFs at high magnification [Fig. 2(c)] demonstrated the uniformity and compactness of the zeolite walls while a micrograph at low magnification [Fig. 2(d)] reveals the high fidelity of HZFs maintaining the original carbon fibrous morphology. The

improvement under step voltage can be ascribed to better matching between the motion of nanozeolites towards the cathode and the lateral motion on the cathode.⁵ The non-conducting nanozeolites deposited on the cathode under 1 V might reduce the voltage drop over the suspension,⁸ so weakening the actual effect of the later application of 2 V so as to slow down the velocity towards the cathode.

The XRD spectrum of carbon substrates shows the pattern of an amorphous phase. However characteristic peaks of silicalite-1 occurred in patterns of ZCFs and only peaks ascribed to silicalite-1 appeared in patterns of HZFs. IR spectra of ZCFs and HZFs further confirm that the carbon fibers have been coated by nanozeolites and HZFs are solely composed of silicalite-1 particles.

Our research has shown that the EPD technique can be employed to assemble nanozeolite particles conveniently and effectively. Uniform zeolite coated fibers have been fabricated by this method and after removal of the substrates, hollow zeolite fibers with ultra-thin walls composed solely of nanozeolites can be obtained. Currently, the preparation of zeolite materials with other structures by electrophoretically assembling various nanozeolites and the applications of zeolite coated fibers as well as hollow zeolite fibers are under way in our laboratory.

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