Size Control of ZnO Nanofibril within Template by Electrophoretic Deposition

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A facile approach was proposed to synthesize uniform ZnO nanofibril with tunable dimension as a function of the template size by using electrophoretic deposition (EPD) process. A mathematical model describing the interaction and coagulation of ZnO nanoparticles within the anodic alumina membrane (AAM) channel environment during EPD is presented, and the related deposition mechanism, morphology, and dimension of the ZnO nanofibril were also discussed. The result shows that the diameters of the fabricated ZnO nanofibrils are uniform and their values are close to the theoretically predicted values for different AAM channel sizes.

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Results and Discussion

The TEMs of ZnO nanofibril prepared in the AAM template with diameters of 50, 100, and 200 nm, respectively, by EPD process are shown in Fig. 1. It is interesting to find that the synthesized nanofibril locates and grows in the center of the cylindrical alumina pore with diameters of about 15.0, 33.4, and 60.0 nm, respectively. It also shows that the ZnO nanofibril is uniform and highly aligned parallel to the channel wall. In a preliminary study, the zeta potential value obtained at the pH value used here demonstrates that the particles are positively charged. Besides, the pore walls of the AAM were also reported to be positively charged. Therefore, the nanofibril is deposited from the center of the AAM channels due to the force balance between particles and channel walls. Similar phenomenon has been reported for the preparation of TiO₂ nanowires by electrochemical deposition, where the nanowires are first formed in the center of the pore and then extend to the pore wall. Although we have successfully synthesized nanofibril arrays within the AAM template, the fundamental electrokinetics and mechanisms for the deposition of nanofibril arrays through a single closed cylindrical channel of AAM are still not completely understood yet. Hence, the suspension flow, electric field, and mass transfer problems within the AAM template by EPD process will be discussed.

By EPD process, application of an electric field to a suspension of charged particles contained in a single closed cylindrical nanochannel of AAM with charged wall results in electrophoretic movement of ZnO nanoparticles and electro-osmotic flow of the fluid medium. The equilibrium velocity of particles is determined by forces acting on the particles. Generally, a successful deposition is achieved when the magnitude of the force to drive suspended particles by electric field is greater than the natural forces of gravity.

In recent years, arrays of nanoscale one-dimensional materials have stimulated great interest and constituted one of the most important frontiers in materials science because of their basic scientific research and potential technological applications. Many attempts have been devoted and applied to the synthesis of one-dimensional nanostructured materials.7-9 Template-mediated synthesis is another important frontiers in materials science because of their basic scientific research and potential technological applications. Many attempts have been devoted and applied to the synthesis of one-dimensional nanostructured materials.1,2 Template-mediated synthesis is another fabrication method for the synthesis of nanostructured arrays of rods, wires, fibers, and tubules of the desired materials within the pores of template.3 Because the porous membranes are easily fabricated with a large range of possible pore diameters adjusted by variation of the experimental anodization conditions, this provides a simple technique for preparing nanowires with the desired diameters.

ZnO is a wide band gap semiconductor, which is suitable for low-voltage and short-wavelength optoelectronic applications. A number of different techniques, such as sol-gel deposition, electrochemical deposition, and chemical vapor deposition, have been proposed to synthesize ZnO nanowire array by template-mediated method.4-5 In our previous study,6,8 the effective and controllable processes combining the synthesis of ZnO nanoparticles and colloidal preparation and electrophoretic deposition (EPD) of ZnO nanowire arrays in anodic alumina membrane (AAM) template were reported. This method allows combination of the advantages of the colloidal process, including diminishing agglomeration and defect populations, and the advantages of EPD, such as the fast and controlled kinetics and application as a materials general process. EPD process has been widely applied for coatings and laminated materials in the micrometer size region.10-11 However, few studies have focused on the electrokinetics and mechanisms of nanoparticles within template by EPD process. For these reasons, a mathematical model describing electrokinetically driven nanoparticles transport and deposit within AAM channel under the influence of electric field and interaction force within this channel environment is presented in this article. In addition, the theoretical equation describing the relationship between the synthesized nanofibril dimension and channel size by EPD process is also discussed.

Experimental

The synthesis of nanometer-sized ZnO colloidal suspensions for EPD in this study followed the method of Bahmann and Hoffmann13 and high purity 2-propanol (99.5%, ACS reagent grade) was used as a suspension solvent to decrease water dissociation and gas evolution during EPD process. From the X-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis, the wurtzite ZnO phase is obtained and the average particle size is about 4.8 nm.14 The AAM (Anodisc, Whatman) was commercially available and characterized with 50, 100, and 200 nm pore diam. The density of pores in AAM fell within the range of 10⁹-10¹¹ pores/cm². For the EPD process, platinum sheets were used as the anode, and an AAM attached to a Cu foil as the cathode. The electrodes were set parallel to each other with a separation distance of 2 cm and immersed into the ZnO suspension kept at a constant temperature during EPD. ZnO nanowire arrays were deposited at 30 V using a regulated dc power supply. After deposition, samples were heat-treated at 400°C for 5 h. Zeta-potential of ZnO nanoparticles was measured by Zetasizer 300HS equipment (Malvern, UK). The morphology of ZnO nanofibril was observed using TEM (JEOL AEM-3010). For TEM analysis, the specimens were prepared by dissolving the assembly with 0.5 M NaOH solution, then dispersed the released ZnO nanofibrils in alcohol by ultrasonic agitation, and then dropped it onto carbon-coated copper grids for observation. The diameter of the deposited nanofibril was determined by averaging several pieces of samples prepared under identical experimental conditions. The error to the average value of the diameter of deposited nanofibril was also determined.

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By EPD process, application of an electric field to a suspension of charged particles contained in a single closed cylindrical nanochannel of AAM with charged wall results in electrophoretic movement of ZnO nanoparticles and electro-osmotic flow of the fluid medium. The equilibrium velocity of particles is determined by forces acting on the particles. Generally, a successful deposition is achieved when the magnitude of the force to drive suspended particles by electric field is greater than the natural forces of gravita-
tion, buoyancy, and friction on the particles. Besides, the fluid velocity will vary with the distance, \( r \), near the surface of the particles. Therefore, the observed velocity, \( v(r) \), of a nanoparticle in the channel of AAM template is the sum of the electrophoretic velocity of the nanoparticle, \( v_p \), and the velocity of electroosmotic flow of the local fluid, \( v_{\text{osm}}(r) \). The velocity equation can be expressed as

\[
v(r) = v_p + v_{\text{osm}}(r)
\]

Mattson\textsuperscript{15} has shown that for the flow in a single closed capillary the observed velocity \( v \) of a nanoparticle is related to its distance, \( r \), from the axis of the tube channel by the expression

\[
v(r) = v_p + v_{\text{osm}} \left( \frac{2r^2}{R^2} - 1 \right)
\]

where \( v_{\text{osm}} \) is the electroosmotic velocity and \( R \) is the radius of the nanochannel size. Solution of Eq. 2 shows that there is a stationary layer, where electro-osmotic and compensatory flows cancel each other, occurred without a net flow at a distance when \( r = r_s = 0.707R \) from the axis of the tube channel. The \( r_s \) is the related distance for nanoparticle from the channel axis to the stationary layer. Only at the stationary layer the measured velocity is the true electrophoretic velocity of the nanoparticle independent of electroosmosis. Dividing all terms in Eq. 2 by the electrical field strength, the observed particle mobility vs. location relative to channel center is shown in Fig. 2. The result shows that the observed particle mobility is a parabolic and symmetric distribution about the AAM channel axis as shown in Eq. 2. Such a parabolic profile occurs in the closed channels due to the channel wall electroosmosis in one direction being compensated by a return flow of fluid down the center of the channel in the opposite direction. The point at which the two fluid flows cancel each other is called the stationary layer. The intervening space between the channel wall and the stationary layer is the stationary phase, \( x = 0.293R \).

As mentioned above, both the particles and channel surfaces carry uniform positive charges in suspension. As such, when they...
are brought into contact with electrolyte solution, there are two electrical double layers (EDL): one is surrounding the particle and the other is next to the channel wall surface. According to the Gouy-Chapman theory, the double layers formed at the surface are composed of a low-mobility dense packed layer of absorbed anions and a mobile layer of associated cations. Recently, advances in the understanding of the EDL and EPD deposition mechanisms have come from the application DLVO (Derjaguin-Landau-Verwey-Overbeek) theory of colloidal stability. The DLVO theory considers two main forces: the Van der Waals’ attraction and coulombic double-layer repulsion. The applied electric field causes a directional force to drive the positively charged particles toward the negatively charged electrode and overcome the repulsive particle-particle electrostatic interactions. Therefore, the electrically charged attraction makes a contribution to particle coagulation and formation of the packing structure within the AAM electrode under the influence of the electric field. Repulsion or steric hindrance is achieved by the interaction of channel surface EDL and electro-osmotic flow in the stationary phase with the nanoparticles. It has been reported that the migration velocity of the fluid components in the stationary phase is more slowly than in the bulk mobile phase due to the higher resistance to mass transfer in the stationary phase. Therefore, it is assumed that the steady state and successful deposition occur between two stationary phases, where the total interaction between colloidal particles and the stationary phase reaches the equilibrium state for ZnO particles to deposit within the AAM channel.

Because the channel is one-side closed, the overall net volume flow ($\Delta V$) between two stationary phases is zero according to above assumption.

$$\Delta V = V_{in} + V_{out} = V_p + V_{z}(y) = 0$$  \[3\]

where $V_z(y)$ is the volume of fluid expelled by deposited particles. The radius of volume transport, $y$, due to fluid expelled is equal to the theoretical radius of the deposited nanofibril. The schematic diagram of deposition volume fraction within AAM channel is illustrated in Fig. 3. The velocity $v$ of a suspended particle in an electric field $E$ is given by

$$v = \mu_p E$$  \[4\]

where $\mu_p$ is the mobility. For particles that are much smaller than the Debye length, the electrophoretic mobility $\mu_p$ is given by Huckel formula

$$\mu_p = \frac{2\varepsilon_0\varepsilon_h \zeta_p}{3\eta}$$  \[5\]

In this equation, $\varepsilon_0$ is the permittivity of free space, $\varepsilon_h$ the dielectric constant of solvent, $\zeta_p$ the zeta potential of particle and $\eta$ the viscosity of the solution. Besides, the electrosomotic mobility $\mu_{osm}$ is

$$\mu_{osm} = \frac{2\varepsilon_0\varepsilon_h \zeta_w}{3\eta}$$  \[6\]

where $\zeta_w$ is the zeta potential of channel wall surface. The fluid flow through the capillary follows Poiseuille’s law and the fluid velocity at the radial distance $y$ in a single-closed channel of radius $r_s$ as shown in Fig. 3 is

$$v(y) = \frac{\Delta p}{4\eta} \left( y^2 - \frac{r_s^2}{2} \right)$$  \[7\]

where $\Delta p$ is counter pressure gradient. In this study, we consider the flow, electric field, mass transfer, and deposition issues in AAM channels. Note that when the nanofibril was deposited within the channel there was a boundary interaction region around the tip of the deposited nanofibril where the fluid flows. However, it has been reported that a fluid passing through the tip of the growing fiber will produce a relatively stagnant boundary layer in a cylindrical channel by which the materials carried by flow are expected to be trapped. The result is an increased rate of deposition of nanofiber at surfaces adjacent to the boundary layer, here the tip of the nanofiber. Therefore, it is reasonable to neglect the interrupting effects of the moving boundary between the fluid motion and the deposited nanofibril in Eq. 7. Moreover, it is shown that an electric field is generated in direction transverse to the primary flow direction in a closed channel; in turn, a counter pressure gradient in the direction normal to the primary flow direction is set up. When the fluid transports through a single-closed cylindrical channel, the pressure gradient $\Delta p$ is obtained as

$$\Delta p = \frac{8\eta v_{osm}}{r_s^3}$$  \[8\]

where $v_{osm}$ is the electro-osmotic velocity. Therefore, substituting Eq. 4-8 into Eq. 3, we have

$$\Delta V = V_p + V_z(y) = \int_0^y 2\pi y v(y) dy - \int_0^y 2\pi y v_p(y) dy = 0$$  \[9\]

After the calculation of Eq. 9, the solution can be written as

$$y = \sqrt{\frac{3r_s^2 (v_p + v_{osm})}{2v_{osm}}}$$  \[10\]

Table I. A comparison of experimental and theoretical results for the thickness of stationary phase and the nanofibril diameter with different channel sizes.

<table>
<thead>
<tr>
<th>Channel size (nm)</th>
<th>Stationary phase (nm)</th>
<th>Experimental diameter (nm)</th>
<th>Theoretical diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>7.3</td>
<td>15.0 ± 0.5</td>
<td>15.1</td>
</tr>
<tr>
<td>100</td>
<td>14.7</td>
<td>33.4 ± 1.0</td>
<td>30.3</td>
</tr>
<tr>
<td>200</td>
<td>29.3</td>
<td>60.0 ± 3.0</td>
<td>60.5</td>
</tr>
</tbody>
</table>

Figure 3. Schematic diagram of deposit contour within AAM channel.
using the following values: \( \varepsilon_i = 18.29, \eta_w = 25.0 \text{ mV}^{14} \eta = 2.3 \text{ mPa s}^{30} \zeta_w = 28.3 \text{ mV}, l = 6 \mu \text{m}, E = 30 \text{ V}, \) and \( r_i = 17.7, 35.4, \) and \( 70.7 \text{ nm} \) when \( r_i \) are 50, 100, and \( 200 \text{ nm}, \) respectively. From the data presented in Table 1, it can be seen that the average nanofibril diameter of experimental results well matches the theoretical ones. In our previous study, although the minimal applied voltage required to drive nanoparticles into the template will change with the channel size, the difference in diameter of the synthesized nanofibril is not evident with the applied voltage at the same channel size. Therefore, we can prepare very smooth and uniform nanofibril arrays in the center of the AAM channel by EPD process.

Zhang et al.\(^{15,16}\) have reported that the preparation of TiO\(_2\) nanofibrils within the AAM template with the diameters of 45 nm, where the nanofibrils were first formed in the center of the pore and with the diameter of 15 nm. It can be found that the result reported by Zhang et al. is very close to that calculated from Eq. 10. It means that the equation presented in this study is useful in calculating the nanofibril diameter changed with the channel sizes of the template. However, there are some potential limitations to deposit nanoparticles within nanoporous membranes. For instance, from Eq. 8 we know that the value of counter pressure increases significantly with the decreasing channel size. Therefore, it is not easy to synthesize ZnO nanofibril in the pores of AAM channel less than 50 nm. This may be due to the high counter pressure and/or slow diffusivity for particles to deposit within the small size of AAM channel, even with an applied electric field. Besides, wall effects on the fluid flow properties cannot be neglected when the channel-to-particle diameter ratio is less than 30.\(^{1} \) Furthermore, the EDL overlap may occur and inhibit mass transport when the size of the flow channel is not significantly greater in magnitude than the EDL thickness.\(^{32} \) As such, there are many issues to be addressed for a more detailed understanding of the related parameters that affect the deposition behavior and nanofibril diameter, and the work is currently underway.

Conclusions

In summary, we report a facile method for the fabrication of ZnO nanofibril with tunable dimension as a function of the template size using EPD. The deposition electrokinetics and characteristics of the ZnO nanofibril within the AAM are well documented. A mathematical analysis of the mass transport within the template channel depends on the net force equilibrium between charged particles and two stationary phases. The electric driving force acting on the ZnO particles deposited in the center of the channel is balanced against the steric repulsion by EDL and electro-osmotic flow within the stationary phase. Therefore, by calculating the dimensions of the stationary layer relative to the channel diameter, ZnO nanofibril dimension can be determined. Moreover, by varying the size of template, the desired size of the nanomaterial can be easily obtained.

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References