Supplementary Information

P(VDF-TrFE) ferroelectric nanotube array for high energy density capacitor applications

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Temperature effect on the silver layers deposited on AAM template by electroless plating

In this work, electroless plating method was used to deposit conductive silver layers into the AAM template and the inner surface of the P(VDF-TrFE) nanotubes as the bottom and top electrodes for electrical testing. It was found that temperature is a critical factor determining the silver deposition rate, and also has a significant effect on the morphology of the resulting silver layer. Therefore, the deposition temperature effect on silver electroless plating and wetting behavior of silver plating solution to AAM template and nanotube inner surface were studied by both theoretical and experimental approaches.

The silver electroless plating reaction is expressed as below:

$$RCHO + 2[Ag(NH_3)_2]^+ + 2OH^- \xrightarrow{k} RCOOH + 2Ag\downarrow + 4NH_3 + H_2O \qquad (1)$$

The temperature effect on the reaction rate can be calculated using Arrhenius equation:

$k = A e^{-Ea/RT}$ (2)

where k is the reaction rate, A is a constant depending on the reaction, Ea is the activation energy, R is the gas constant, T is the reaction temperature.

According to Equation (2), the effect of temperature on reaction rate k can be calculated using Eq.3 when the temperature is changed from T_1 to T_2.

$$\ln\left(\frac{k_2}{k_1}\right) = \left(\frac{Ea}{R}\right) * \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (3)$$

In this equation, R=8.314 $J \cdot mol^{-1} \cdot K^{-1}$; For the silver electroless plating reaction, Ea=57 $kJ \cdot mol^{-1}$.

The silver electroless plating process was carried out at three different temperatures: 0 ^oC, 20 ^oC, and 50 ^oC. The change in relative reaction rate was calculated using Eq.3 and listed in Table S1.

Table S1. Relative reaction rate of silver electroless plating process at different temperatures

Temperature (K)	Relative reaction rate
273	k_0
293	k_1/k_0 =5.54
323	k_2/k_1 =8.79

According to the calculation, the reaction rate increases 5.54 times when the temperature increases from 0 ^oC to 20 ^oC and another 8.79 times from 20 ^oC to 50 ^oC. At a slightly elevated temperature, much more rapid deposition of silver may lead to large particle size and rough surface of the silver layer，which was not desirable as electrodes for the nanotubes. On the other hand, at a low temperature, it will take too much time to deposit a continuous silver layer due to the very low deposition rate.

Figure S1 shows the SEM images of silver layer on AAM surface deposited at different temperatures, which confirmed the critical temperature effect on the silver deposition rate and resulting morphology. Figure S1(a) shows the AAM template before the silver plating. As shown in Figure S1(b), the deposition at 0^oC after 25 minutes could not form a continuous silver layer due to the slow deposition rate. At 20 ^{o}C, a continuous silver layer with a thickness of tens of nanometer was formed on the surface, as shown in Figure S1(c). The surface of silver layer deposited at 50 ^{o}C was relatively rough due to the further improved deposition rate, as shown in Figure S1(d). In this work, the deposition temperature is controlled at 20 ^{o}C for a suitable deposition rate as well as a relative smooth morphology of the obtained silver layer.

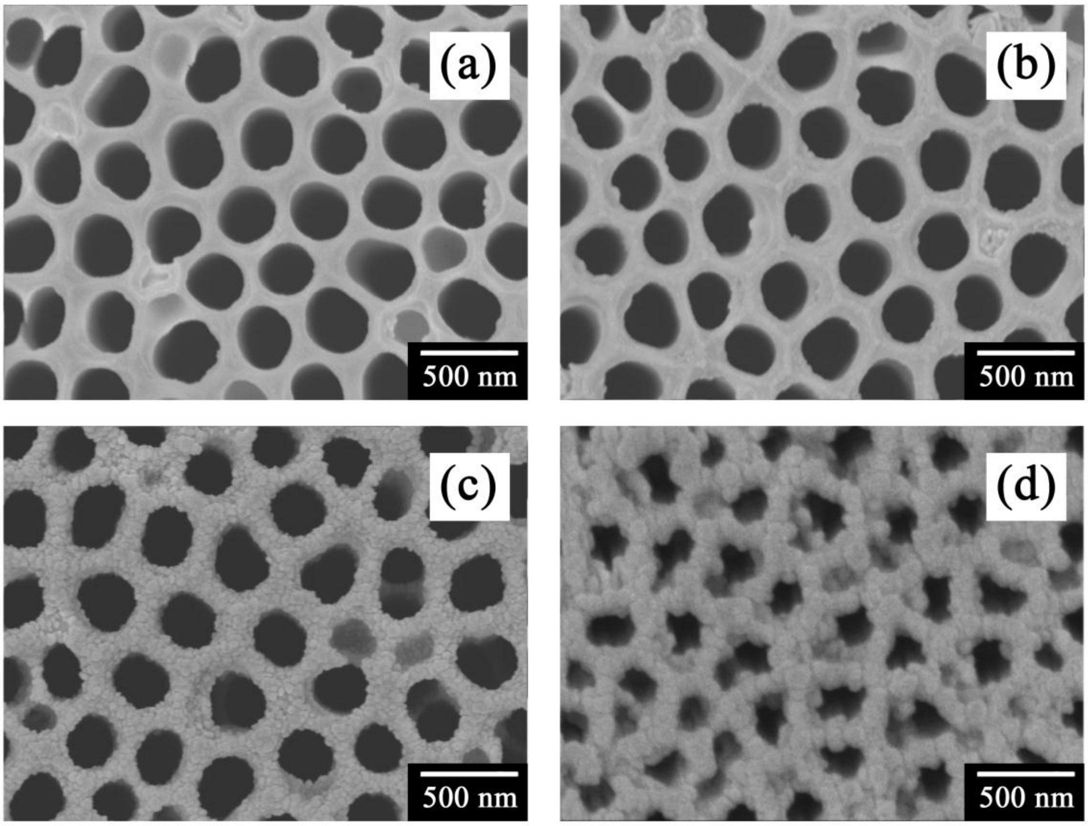

Figure S1. SEM images of (a) bare AAM template, and AAM with the silver layer electroless deposited at (b) 0 ^{o}C, (c) 20 ^{o}C, and (d) 50 ^{o}C, for 25 minutes.