Supplementary Information:
Poly(arylene ether nitrile) Composites with Surface-Hydroxylated Calcium Copper Titanate Particles for High-Temperature-Resistant Dielectric Applications

Junyi Yang, Zili Tang, Hang Yin, Yan Liu, Ling Wang, Hailong Tang and Youbing Li

S1. Synthesis of Poly(arylene ether nitrile) (PAEN)

In a typical synthesis procedure, 2,6-Dichlorobenzonitrile (22.0 g, 128 mmol), bisphenol A (29.2 g, 128 mmol), anhydrous K$_2$CO$_3$ (35.4 g, 256 mmol), NMP (85 mL), and toluene (35 mL) were added into a 250 mL three-neck round bottom flask equipped with a Dean-Stark trap, condenser, mechanical stirrer, and thermometer. The system was heated to 140–160 °C to remove water from the reaction by azeotropic distillation with toluene for 3 h. Toluene was then removed by distillation and the temperature was gradually raised to 190–200 °C. The system was kept stirring for about 5 h until its viscosity did not increase any more. Afterwards, the reaction mixture was poured into deionized water to precipitate the polymer. The precipitate was crushed and then poured into 1 L of diluted HCl solution in order to remove the excess K$_2$CO$_3$. Finally, the collected polymer was washed five times with boiling deionized water and dried in a vacuum oven at 130 °C for 12 h to produce a white solid.

S2. Theoretical Calculation by Lichtenecker’s Logarithmic Mixture Model

The relationship between the dielectric properties of a two-phase mixture and those of each phase in the mixture can be expressed by Lichtenecker’s logarithmic mixture model [1].

$$\log \varepsilon = f_1 \log \varepsilon_1 + f_2 \log \varepsilon_2$$

where \(\varepsilon\) is the complex permittivity of the composites, \(\varepsilon_1\) and \(f_1\) are the dielectric permittivity and volume fraction of the polymer matrix, and \(\varepsilon_2\) and \(f_2\) are the dielectric permittivity and volume fraction of the inorganic filler, respectively.

Dielectric permittivity of PAEN: \(\varepsilon_1 = 2.86\) (1 kHz)  
Density of PAEN: \(\rho(\text{PAEN}) = 1.18\)

Dielectric permittivity of h-CCTO: \(\varepsilon_2 = 114\) (1 kHz)  
Density of h-CCTO: \(\rho(\text{h-CCTO}) = 5\)

For example: PAEN/h-CCTO composites with 15 wt% h-CCTO particles

Assumed total mass: \(m = 100\)

\(m(\text{PAEN}) = 85\)  \(m(\text{h-CCTO}) = 15\)

\(V(\text{PAEN}) = m(\text{PAEN}) / \rho(\text{PAEN}) = 72\)

\(V(\text{h-CCTO}) = m(\text{h-CCTO}) / \rho(\text{h-CCTO}) = 3\)

\(f_1 = \frac{V(\text{PAEN})}{V(\text{PAEN}) + V(\text{h-CCTO})} = 0.96\)

\(f_2 = 1 - f_1 = 0.04\)

Calculated by Equation (1): \(\varepsilon = 3.31\)
Table S1. Experimental and theoretical dielectric permittivity of PAEN/h-CCTO composites.

<table>
<thead>
<tr>
<th>Mass fraction of h-CCTO</th>
<th>0 wt%</th>
<th>15 wt%</th>
<th>30 wt%</th>
<th>45 wt%</th>
<th>60 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental values</td>
<td>2.86</td>
<td>3.52</td>
<td>4.16</td>
<td>5.11</td>
<td>6.31</td>
</tr>
<tr>
<td>Theoretical values</td>
<td>2.86</td>
<td>3.31</td>
<td>4.01</td>
<td>5.20</td>
<td>7.48</td>
</tr>
</tbody>
</table>

Figure S1. Schematic synthesis procedure of poly(arylene ether nitrile).

Figure S2. Field emission scanning electron micrograph (FE-SEM) images of (a) CCTO and (b) h-CCTO particles.
Figure S3. Digital photo of dispersions of pure CCTO and h-CCTO particles in ethanol after standing for four hours.

Figure S4. Cross-sectional SEM image of PAEN composites with 15 wt% non-hydroxylated CCTO particles.

Figure S5. Electrical conductivity of PAEN/h-CCTO composite with 30 wt% h-CCTO content as a function of temperature.
Figure S6. TGA and DTG curves of h-CCTO particles.

Reference: