

Supporting Information

An Ultralow- k Dielectric Derived from Fluorinated Polybenzoxazole Composite Film with Yolk-Multishell Mesoporous Silica Nanostructures

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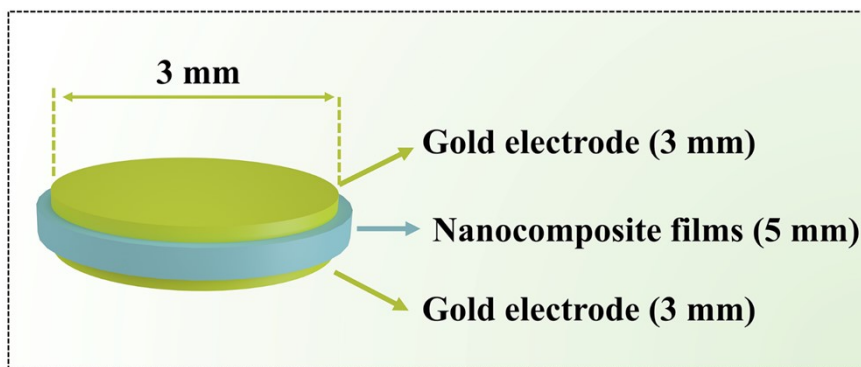


Fig. S1 Capacitor model diagram for dielectric constant measurement.

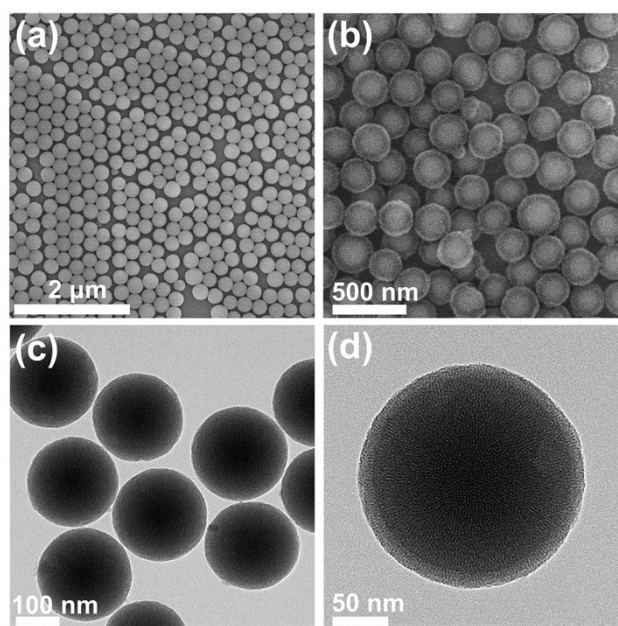


Fig. S2 (a) FESEM images of CSSs; (b) FESEM images of YS-CSSs@1S-mSiO₂; (c, d) TEM images of MSN.

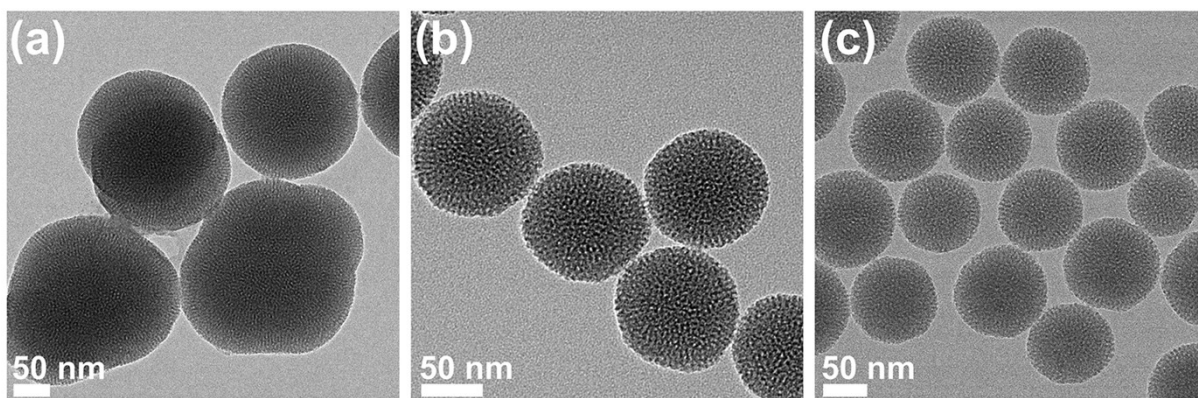


Fig. S3 Preparation of CSSs of different sizes at different stirring speeds (a) 250 nm (1100 r/min); (b) 110 nm (900 r/min); (c, d) 90 nm (700 r/min).

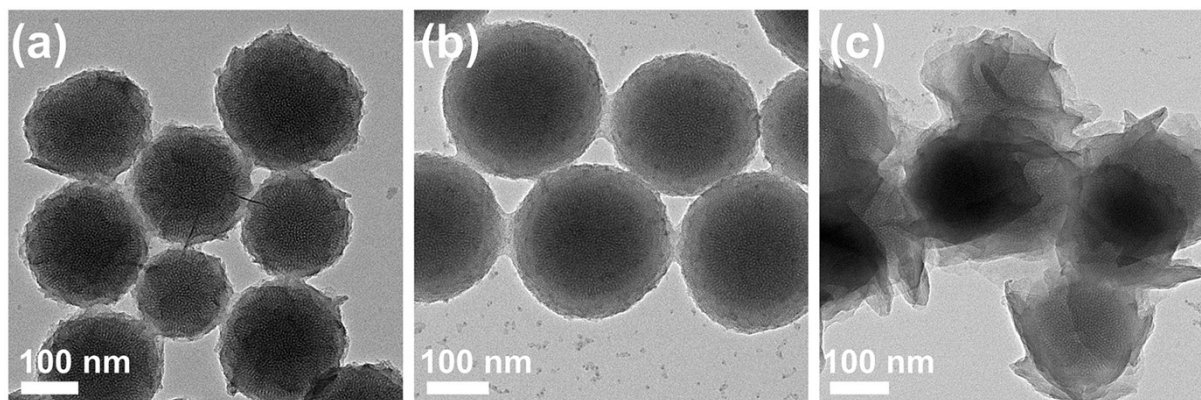


Fig. S4 Volume ratio of TEOS/C₁₈TMS (a) 5:1; (b) 5:2; (c, d) 5:3.

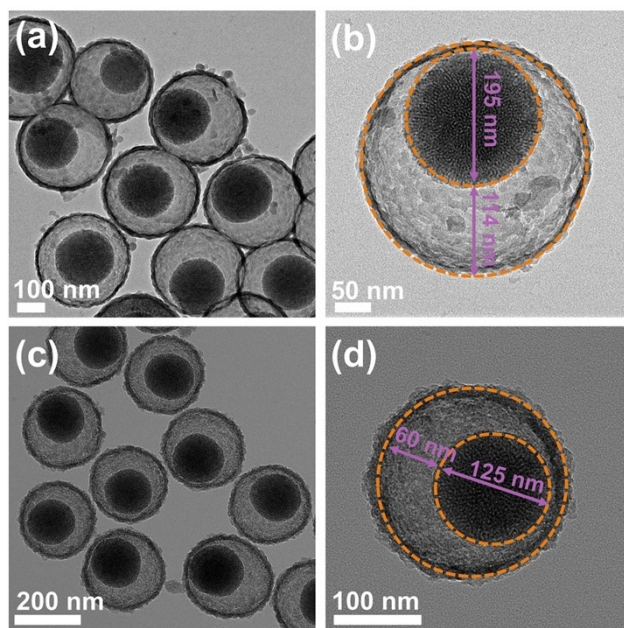


Fig. S5 YS-CSSs@1S-mSiO₂ with different diameters and cavity size. (a, b) 325 nm (114 nm); (c, d) 240 nm (60 nm).

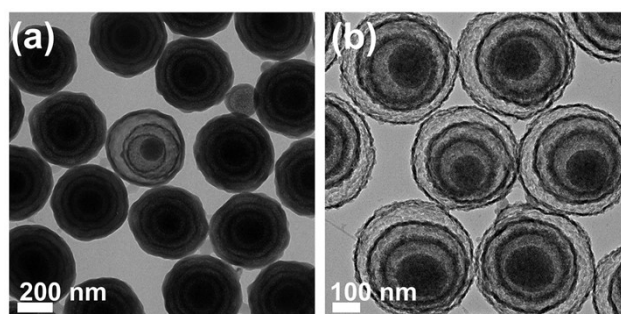


Fig. S6 Preparation of silica using different amounts of HF. (a) 0.1 mL ; (b) 0.2 mL.

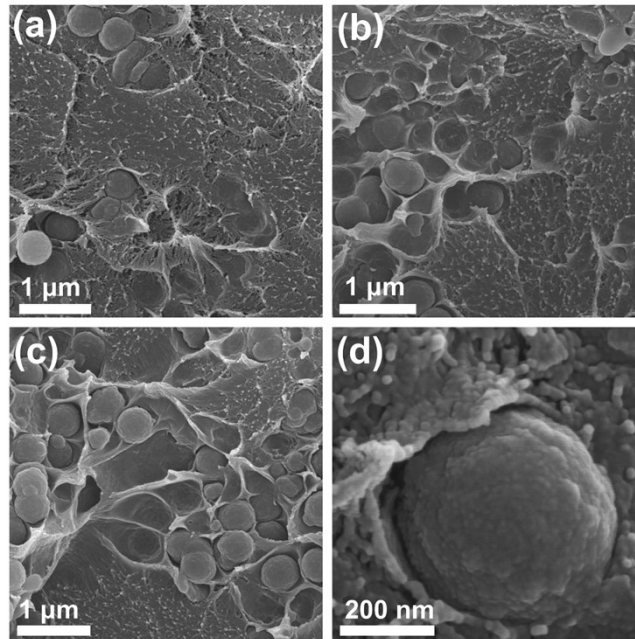


Fig. S7 FESEM images of nanocomposite films with (a)2 wt.%, (b)4 wt.%, (c)6 wt.% of YS-CSSs@3S-mSiO₂ hollow nanospheres, (d) a close-up FESEM image.

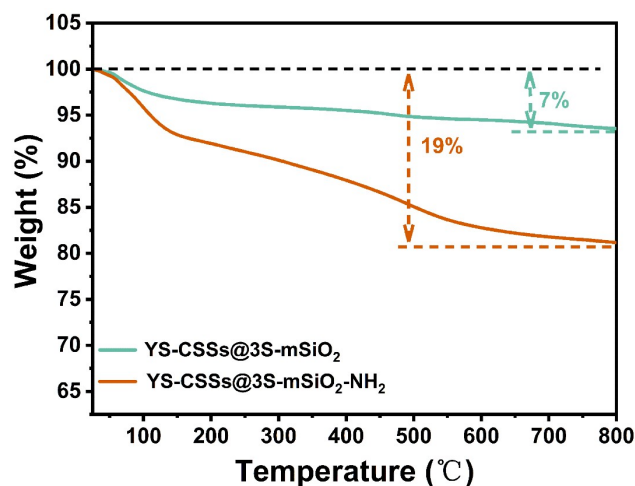


Fig. S8 TGA curves of YS-CSSs@3S-mSiO₂ and YS-CSSs@3S-mSiO₂-NH₂ nanoparticles.

We performed TGA tests on YS-CSSs@3S-mSiO₂ nanoparticles and YS-CSSs@3S-mSiO₂-NH₂ nanoparticles. As shown in Fig. S8, the thermal weight loss of YS-CSSs@3S-mSiO₂ nanoparticles and YS-CSSs@3S-mSiO₂-NH₂ nanoparticles was 93% and 81% respectively over the temperature range of 0-800 °C. The 12% increase in weight loss of YS-CSSs@3S-mSiO₂-NH₂ nanoparticles was due to the thermal degradation of the organic groups. We believe that the above results are further evidence of the success of the functionalization of YS-CSSs@3S-mSiO₂ nanoparticles with amino groups.

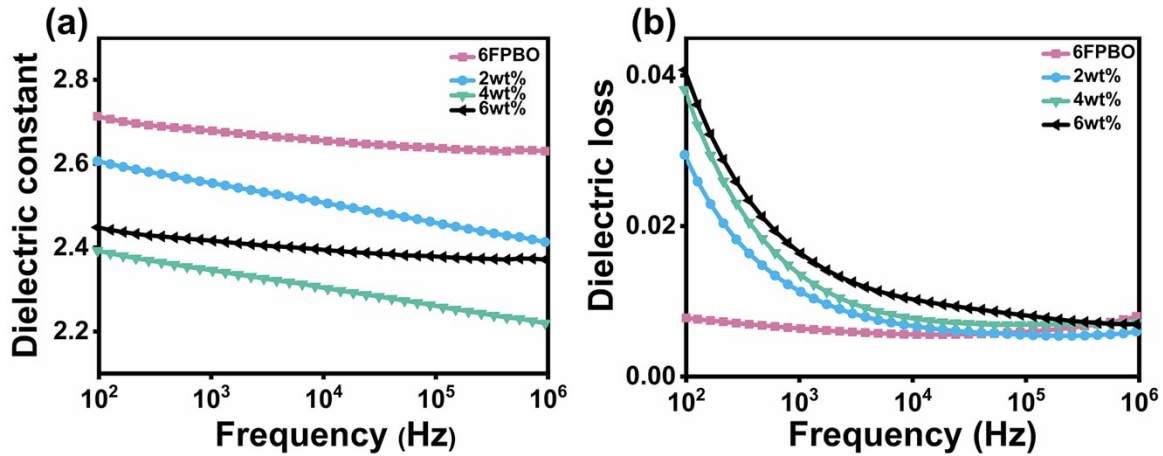


Fig. S9 Frequency dependence of k (a) and dielectric loss (b) of the YS-CSSs@3S-mSiO₂/6FPBO nanocomposite films at room temperature. YS-CSSs@3S-mSiO₂ nanoparticles are not modified by amination functionalization.

The k values of the composites with different YS-CSSs@3S-mSiO₂ nanoparticle contents decrease with increasing frequency at room temperature (Fig. S9). The k value also decreases with increasing nanoparticle content, among which the k value of the 4 wt.%-YS-CSSs@3S-mSiO₂ composite is the lowest (2.34) at room temperature and 1 kHz, However when the nanoparticle content was further increased to 6 wt.%, the dielectric constant of the composites increased this was mainly attributed to the agglomeration of the nanoparticles, in agreement with the SEM results. The lowest dielectric constant value of the YS-CSSs@3S-mSiO₂/6FPBO nanocomposite films is much higher than 8 wt.%-YS-CSSs@3S-mSiO₂-NH₂/6FPBO nanocomposites. This is mainly due to several reasons: firstly the nanoparticles are not amino-functionally modified, so there is no covalent bonding with the 6FPBO matrix. When the YS-CSSs@3S-mSiO₂ content increases, the nanoparticles cannot be uniformly dispersed in the 6FPBO matrix and are prone to agglomeration thus increasing the dielectric constant. Secondly, the maximum filling of the nanoparticles is only 4 wt.%, with less air introduced, and the resulting dielectric constant is higher, provided that dispersion is guaranteed. Thirdly, the nanoparticles do not interact with the 6FPBO matrix interface, so they cannot restrict the orientation of the polar groups at the interface, resulting in a higher dielectric constant for the composite. Furthermore, the lowest dielectric loss of YS-CSSs@3S-mSiO₂/6FPBO is also

higher than that of the same content of YS-CSSs@3S-mSiO₂-NH₂/6FPBO nanocomposite films. In conclusion, the dielectric properties of the YS-CSSs@3S-mSiO₂/6FPBO nanocomposite films are not as good as those of the YS-CSSs@3S-mSiO₂-NH₂/6FPBO nanocomposite films, demonstrating the importance of amino-functionalization of YS-CSSs@3S-mSiO₂

Table S1 Mechanical properties of the 6FPBO and YS-CSSs@3S-mSiO₂/6FPBO films.

Polymer	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation (%)
Pure 6FPBO	67.4±2.3	1.35±0.07	2.2±0.2
2 wt% YS-CSSs@3S-mSiO ₂ /6FPBO	78.5±2.1	1.76±0.12	2.5±0.2
4 wt% YS-CSSs@3S-mSiO ₂ /6FPBO	68.4±2.7	1.39±0.08	2.3±0.2
6 wt% YS-CSSs@3S-mSiO ₂ /6FPBO	59.3±3.3	1.28±0.13	2.2±0.2
8 wt% YS-CSSs@3S-mSiO ₂ /6FPBO	50.5±4.1	1.19±0.06	2.1±0.2
10 wt% YS-CSSs@3S-mSiO ₂ /6FPBO	41.1±3.3	1.04±0.18	1.9±0.2

The mechanical properties of 6FPBO and YS-CSSs@3S-mSiO₂/6FPBO nanocomposite films are shown in Table S1. With the increase of YS-CSSs@3S-mSiO₂ nanoparticle content, the tensile strength, tensile modulus and the elongation of nanocomposite films increase first and then decrease. When the addition of YS-CSSs@3S-mSiO₂ nanoparticles is 2 wt.%, the composite film reaches 78.5 MPa for tensile strength, while the tensile modulus yields a value of 1.76 GPa with an elongation at break of 2.5%. When compared with pure 6FPBO film, all values show an obvious improvement in tensile strength and tensile modulus (16% and 30% for unstretched and stretched films, respectively), with the elongation at break increasing by 13%. This is mainly because the aminated nanoparticles can be covalently bonded to the 6FPBO matrix, thus enhancing the interfacial interaction and compatibility between the nanoparticles and the matrix and therefore ensuring the uniform dispersion of YS-CSSs@3S-mSiO₂

nanoparticles in the matrix. During the tensile test, to a certain extent, the load can be transmitted to avoid stress concentration, thereby improving the mechanical properties of the composite material. However, when the nanoparticle content continues to increase, the nanofiller will reduce the mobility of the 6FPBO molecular segment, resulting in a certain brittleness of the composite material. When the nanoparticle content is too high, agglomeration will occur, which leads to decreased mechanical properties. Although the mechanical properties of the composites have declined, the nanocomposite films still have excellent mechanical properties.