Supporting Information

Chemically bonding BaTiO3 nanoparticles in highly filled polymer nanocomposites for greatly enhanced dielectric properties

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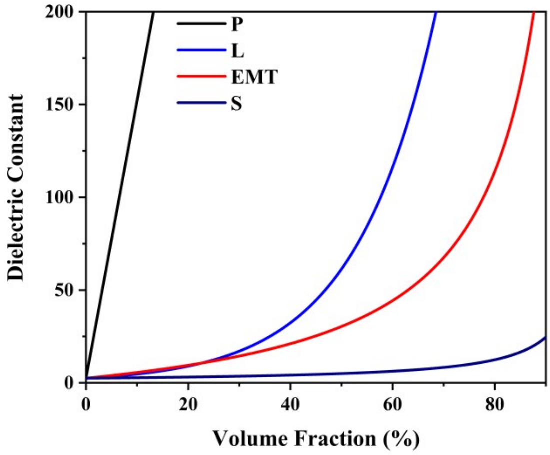

Figure S1 Theoretical calculation curves of Parallel model, Logarithmic model, EMT model and Series model comparing with experimental value.

Table S1 Theoretical models for predicting the dielectric constants of polymer composites

Models	Equation
Parallel model	$\varepsilon = vol_F\%\ \varepsilon_F + vol_M\%\ \varepsilon_M$
Logarithmic model	$\varepsilon = e^{vol_F\% \ln \varepsilon_F + vol_M\% \ln \varepsilon_M}$
EMT model	$\varepsilon = \varepsilon_M\left[1 + \frac{vol_F\%\ (\varepsilon_F - \varepsilon_M)}{\varepsilon_M + n\ vol_M\%\ (\varepsilon_F - \varepsilon_M)}\right]$
Series model	$\varepsilon = \frac{\varepsilon_F\ \varepsilon_M}{vol_F\%\ \varepsilon_M + vol_M\%\ \varepsilon_F}$

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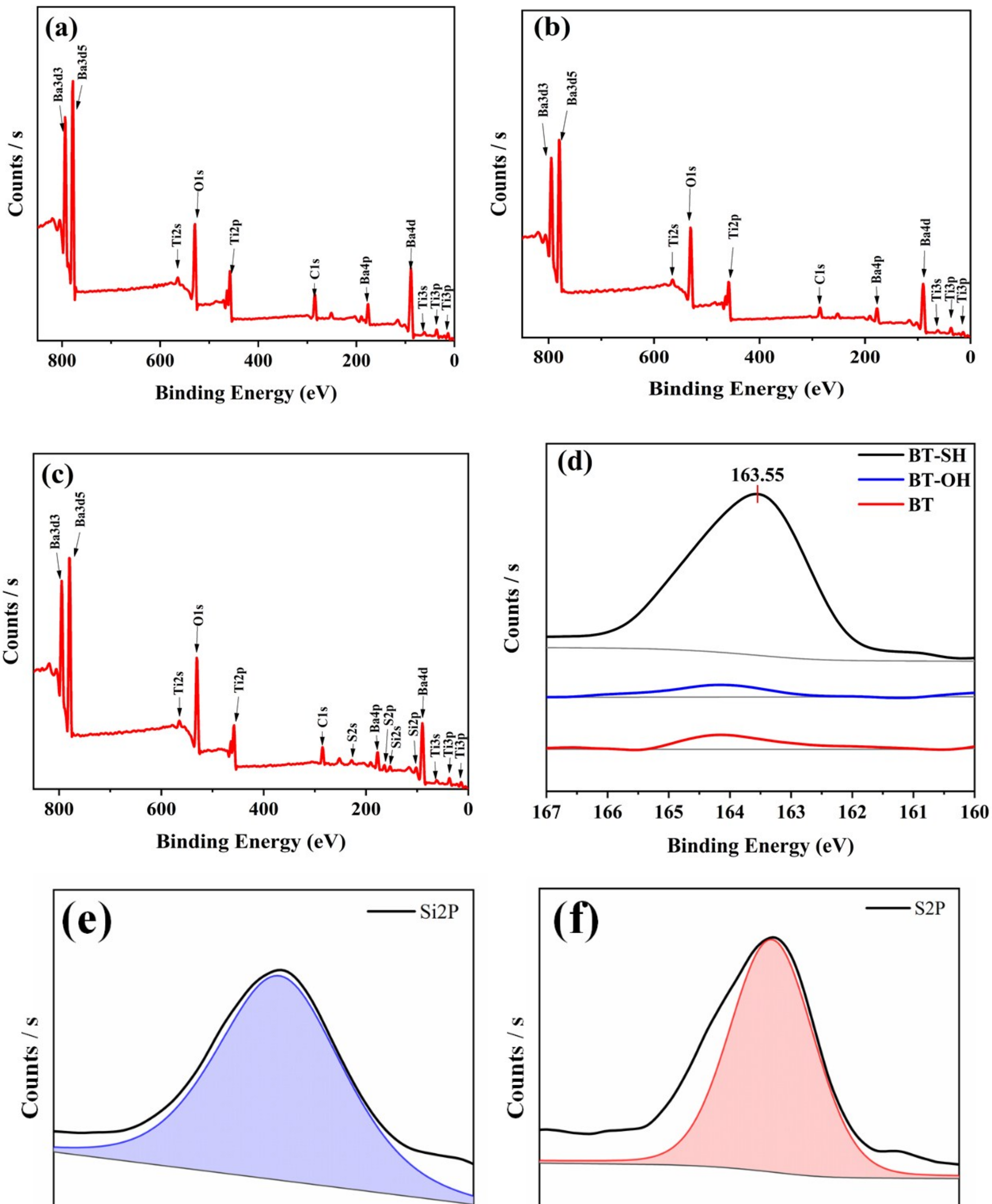

Figure S2 Wide-scan XPS spectra of (a) BT, (b) BT-OH, (c) BT-SH and (d) S2P spectra of BT, BT-OH and BT-SH, (e) Si2p and (f) S2p core-level spectra of the BT-SH surfaces.

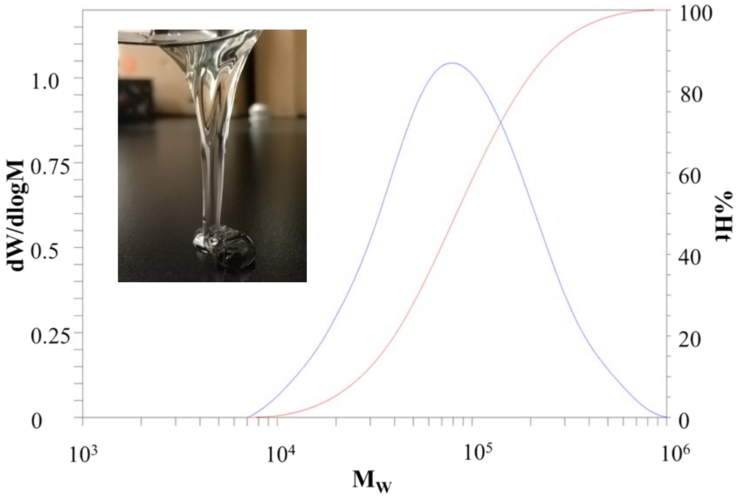

Figure S3 GPC curves of polymethylvinylsiloxane.

Table S2 Molecular parameters of polymethylvinylsiloxane from GPC curves.

	Mp	Mn	Mw	Mz	Mz+1	Mv
PMVSO	79255	57278	118361	224636	355202	106495

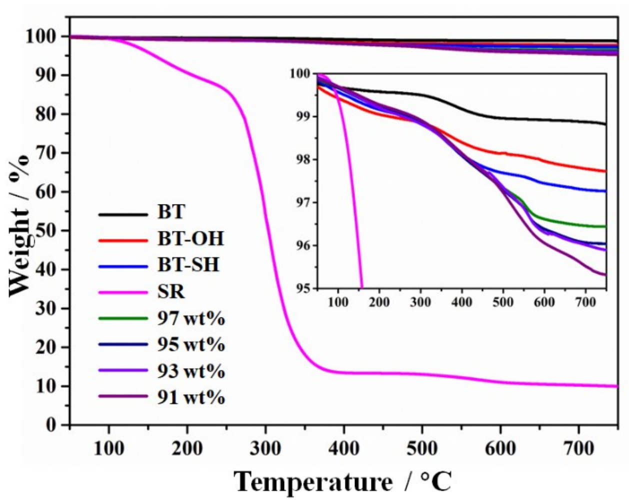

Figure S4 Thermal gravimetric analysis curves of the BT nanoparticles with different surface modifications, neat SR, and the nanocomposites at high BT nanoparticles loading.

Figure S4 depicts the weight changes of BT nanoparticles, neat SR and the nanocomposites with increasing the temperature. The decreasing trend of weight-loss ratios (BT > BT-OH > BT-SH > 97 wt% > 91 wt% > 88 wt% nanocomposites) at 700 °C also suggest the successful modification of BT nanoparticles and fabrication of highly-filled polymer nanocomposites.

The volume fraction of BTs ($vol_1\%$) and SR shell ($vol_2\%$) can be calculated with **Formula S1 and S2**, and mass fraction of BTs ($wt_1\%$) can be calculated with **Formula 3.** Conversion relationship between mass fraction and volume fraction is depicted in **Figure S4 (a)**.

$$vol_1\% = \frac{\frac{4}{3}\pi R^3}{\frac{4}{3}\pi (R+d)^3} \times vol_2\% \quad \textbf{S1}$$

$$vol_3\% = vol_2\% - vol_1\% \quad \textbf{S2}$$

$$wt_1\% = \frac{m_1}{m_1+m_2+m_5} = \frac{m_1}{m_1+m_2} = \frac{\rho_1 vol_1\%}{\rho_1 vol_1\% + \rho_2 vol_2\%} \quad \textbf{S3}$$

Table S3 key parameters for the calculation of volume fraction of voids

Parameter	Set Value	Annotation
1	-	BT nanoparticles.
2	-	SR.
3	-	SR shell.
4	-	SR which fills the void.
5	-	Voids.
C	-	Critical value with $vol_5\%$=0.
max	-	Critical value with $vol_5\%$=25.95%.
R	50nm	The average radius of BT nanoparticles.
d	2nm	The minimum average thickness of the shell layer.
ρ_0	~0	The density of air.
ρ_{BT}	6.08g/cm^3	The density of BT nanoparticles.
ρ_{SR}	1.2g/cm^3	The density of SR.
$Vol_0\%$	74.05%	The space utilization of FCC structure.
n	0.9	the morphology factor of EMT
ε_{BT}	1500	The dielectric constant of BT nanoparticles.
ε_{SR}	2.51	The dielectric constant of SR

One of the closest 3D-packing models of spheres with the equivalent radius is the face-centered cubic (FCC) model, as depicted in **Figure 2 (l),** which has a space utilization of 74.05% and a maximum void volume fraction of 25.95%. The critical volume fraction and mass fraction of BTs can be calculated as:

$$vol_{1C}\% = \frac{\frac{4}{3}\pi R^3}{\frac{4}{3}\pi (R+d)^3} \times vol_0\% = 65.83\%$$

$$wt_{1C}\% = \frac{\rho_1 vol_{1C}\%}{\rho_1 vol_{1C}\% + \rho_2 vol_{2C}\%} = 90.71\%$$

In this study, the nanocomposites are composed of BTs, SR matrix and voids. Their relationship can be described as **Formula S4 and S5**. The volume fraction of voids at a certain BT mass fraction can be calculated with the **Formula S6.** At the maximum void volume fraction, maximum mass fraction of BTs ($wt_{1max}\%$) in certain shell thickness can be confirmed. The next section insights a brief discussion on voids and dielectric constant behavior of the extremely high-filled polymer composites.

$$1 = vol_1\% + vol_2\% + vol_5\% \quad \text{S4}$$

$$1 = wt_1\% + wt_2\% + wt_5\% = wt_1\% + wt_2\% \quad \text{S5}$$

$$\rho_2 vol_2\% = \frac{\rho_1 vol_1\%}{wt_1\%} - \rho_1 vol_1\% = \rho_1 vol_1\% \frac{1 - wt_1\%}{wt_1\%}$$

$$vol_2\% = \frac{\rho_1}{\rho_2} vol_1\% \frac{1 - wt_1\%}{wt_1\%}$$

$$vol_5\% = 1 - vol_2\% - vol_1\% = 1 - vol_1\% \left[1 + \frac{\rho_1(1 - wt_1)}{\rho_2 wt_1}\right] \quad \text{S6}$$

Most of dielectric constant prediction models of polymer composites, like as EMT, are based on continuous structure. EMT model can give a precise prediction of dielectric constant for the polymer composites filled with 0 dimensional fillers, which is indicated in **Figure S5 (b)** and **(c)**. When filler mass fraction is above critical value, void volume fraction cannot be neglected and continuous structures of matrix are damaged.

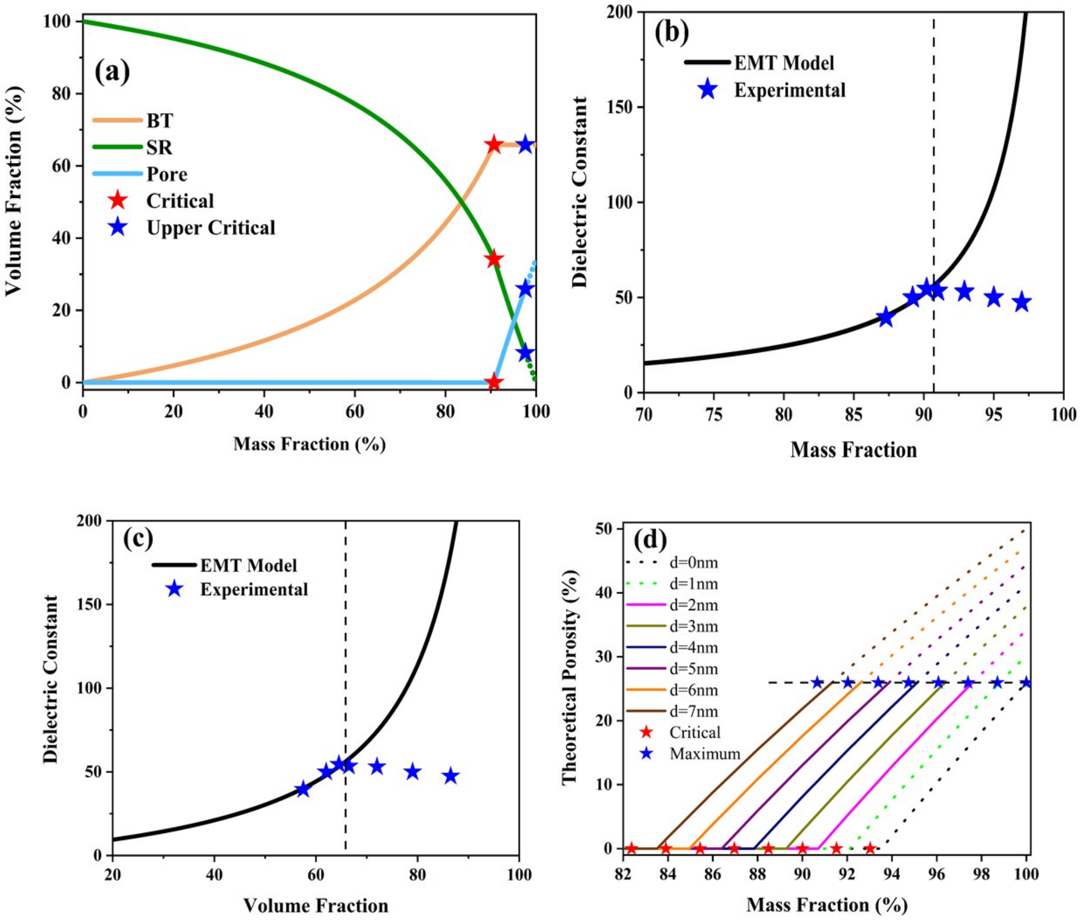

Figure S5 (a) relation between mass and volume fraction of the components (based on BT mass fraction and 2 nm thick shell); (b) EMT model prediction and experiment results (based on mass fraction); (c) EMT model prediction and experiment results (based on volume fraction); (d) critical values of different organic layer thickness.

Table S4 Critical values of the component variation with thickness of organic layer

d/nm	$vol_{1C}\%$	$vol_{2C}\%$	$vol_{3C}\%$	$wt_{1C}\%$	$wt_{1max}\%$
0*	**74.05***	**25.95***	**0***	**93.53***	**100***
1*	**69.78***	**30.22***	**4.27***	**92.13***	**98.81***
2	**65.83**	**34.17**	**8.22**	**90.71**	**97.59**
3	**62.17**	**37.83**	**11.88**	**89.28**	**96.37**
4	**58.78**	**41.22**	**15.27**	**87.84**	**95.12**
5	**55.63**	**44.37**	**18.42**	**86.40**	**93.87**
6	**52.71**	**47.29**	**21.34**	**84.96**	**92.60**
7	**49.98**	**50.02**	**24.07**	**83.51**	**91.32**

Table S5 Representative dielectric properties of polymer nanocomposites with 0 dimensional BT nanoparticles.

Matrix	Filler loading	$\varepsilon_{eff}/\varepsilon_m$	tanδ	E_b/E_m	References
PMMA	35 wt%	1.54	0.028	/	[S1]
Polyimide	50 wt%	2.69	0.016	0.912	[S2]
P(VDF-TrFE-CTFE)	59 wt%	3.25	0.009	0.613	[S3]
PVDF	77 wt%	5.52	0.035	/	[S4]
P(VDF-HFP)	82 wt%	2.62	0.025	0.625	[S5]
PMMA	83 wt%	10.23	0.032	/	[S6]
SR	90 wt %	21.85	0.019	0.797	This work

Note:

PMMA, Poly(methyl methacrylate)

PVDF, Poly(vinylidene fluoride)

P(VDF-HFP), Poly(vinylidene fluoride-cohexafluoropropylene)

P(VDF-TrFE-CTFE), Poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene)

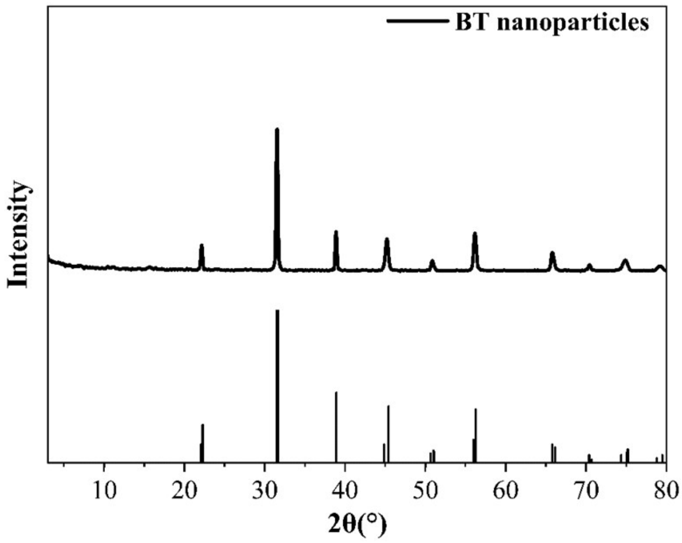

Figure S6 X-Ray Diffraction spectrum of BTs

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