Regulating dielectric performances of Poly(vinylidene fluoride) nanocomposites by individually controlling shell thickness of Core@Double-Shells structured nanowires

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Abstract
The synthesis of core@double-shells structured TiO$_2$@C@SiO$_2$ nanowires (NWs) with variable thickness of carbon inner shell and SiO$_2$ outer shell was achieved by individually controlling the chemical vapour deposition time and amount of silicon precursor added in the sol–gel synthesis. The resultant TiO$_2$@C@SiO$_2$ NWs filled nanocomposites exhibited an excellent dielectric performance with simultaneously improved dielectric constant and suppressed dielectric loss, which could be further regulated by individually controlling the carbon inner shell and SiO$_2$ outer shell thickness. More importantly, the influences of the conductive carbon inner shell and insulated SiO$_2$ outer shell thickness on the dielectric performance of nanocomposites were clearly revealed. The increase of the conductive carbon inner shell thickness would lead to an increase in dielectric constant and loss of nanocomposites, while the insulated SiO$_2$ outer shell exhibited a totally opposite law that the dielectric constant and loss of nanocomposites decrease with increasing SiO$_2$ outer shell thickness. Numerical simulations were also carried out to theoretically verify the relationship between the dielectric loss and SiO$_2$ outer shell thickness. This promising controllable multi-shell structure could be extended to a variety of hybrids to develop high-performance dielectric nanocomposites.

1 | INTRODUCTION

The urgent demand of flexible electrostatic capacitor with high energy storage density and power density has aroused a considerable attention in the field of high dielectric constant (high-$\varepsilon$) polymer nanocomposites comprising polymer matrices and inorganic fillers [1–13]. Numerous efforts have been devoted to improving the dielectric constant of polymer nanocomposites [13–16]. According to the type of fillers used, the strategies employed in previous studies could be mainly divided into two categories [15]. One was to incorporate conductive fillers into the polymer matrix to prepare the percolative nanocomposites, where the high dielectric constant was obtained in the vicinity of the percolation
threshold \( \epsilon \) \([2,9,10,13,17–19]\). However, in spite of high dielectric constant, this kind of composites has too high dielectric loss to be used in practical applications. The other strategy was employing the high-\( \epsilon \) ceramic fillers \([3,20–27]\). Nevertheless, the desirable dielectric constant could be merely obtained at a high filler loading, which would definitely deteriorate the flexibility and electrical breakdown strength of the nanocomposites \([28]\).

Recently, significant efforts have been made to solve the aforementioned issue by developing the core@shell structured fillers \([8,9,12,29–38]\). Generally, two types of core@shell structure have been reported. The first type was conductive fillers or high-\( \epsilon \) ceramic cores coated by an insulated shell \([8,12,29,30,32,33,38–40]\). The direct contact of adjacent fillers was prevented by the insulated barrier interlayer. Thus, the leakage current, caused by the tunnelling effect or direct ohmic contact of the adjacent fillers, would be greatly suppressed, resulting in low losses. This method was first reported by Xu and Wong \([32]\). The amorphous aluminium oxide (Al\(_2\)O\(_3\)) layer, which was obtained from self-passivated of aluminium (Al), acted as an insulated boundary to prevent the contact of Al core. This unique structure endowed the nanocomposites with an extremely low loss of 0.02 at a filler loading as high as 50 wt.% \([32]\). Apart from the conductive metal fillers, carbon nanotubes (CNTs) have also been utilised as the templates for being coated with an insulated shell \([8,33]\). Both the hydrothermal reaction and chemical vapor deposition (CVD) deposition have been used to wrap the CNTs with an amorphous carbon shell to decrease losses and the as-suppressed losses could be further tuned by varying the amorphous carbon thickness \([8]\). For the coating layers of high-\( \epsilon \) ceramic fillers, the SiO\(_2\) and Al\(_2\)O\(_3\) layers were widely selected as the insulated shells due to their synthesis characteristic \([12,38,39,41–43]\). For example, Tang et al. reported that the dielectric loss of calcium copper titanate nanowires (CCTO NWs) filled nanocomposites could be largely suppressed by coating the CCTO NWs core with a SiO\(_2\) insulated shell \([39]\). The coating of barium titanate (BaTiO\(_3\)) NWs (BT NWs) with the Al\(_2\)O\(_3\) shell was reported by Pan et al. and the resultant nanocomposites exhibited an extremely low dielectric loss \([41–43]\). The other type of core@shell structure was adopted by wrapping the ceramic filler core with a conductive shell to introduce polarisable domains and improve the dielectric constant of ceramic filler-based nanocomposites \([9,31,34–37]\). For instance, the dielectric constant of nanocomposites was largely enhanced by employing the core@shell structured BaTiO\(_3\)@Carbon (BT@C) hybrids \([36]\). The similar hybrids synthesised by coating the TiO\(_2\) nano-flowers or TiO\(_2\) NWs with the conductive carbon shell were also adopted to improve the dielectric constant of nanocomposites \([9,37]\).

Nevertheless, the moderate dielectric constant and undesirable high dielectric loss were unavoidably caused by employing the aforementioned two types of core@one-shell strategies, respectively \([22,23]\). Therefore, it is still a huge challenge to simultaneously improve dielectric constant and suppress dielectric loss of nanocomposites via the traditional core@one-shell concept. Recently, the core@multi-shells strategy reported by Huang et al. demonstrated that the dielectric performance of nanocomposites could be really improved by successively grafting the BaTiO\(_3\) nanoparticles with a more conductive polymer inner shell and a more insulated polymer outer shell \([23]\). The confinement of conductive polymer inner shell between the BaTiO\(_3\) core and insulated polymer outer shell endowed the nanocomposites with two additional types of interfacial polarization. Meanwhile, the excellent insulated property of polymer outer shell afforded a low dielectric loss of the polymer nanocomposites. However, the complicated polymerisation procedure for grafting these two kinds of polymer shells onto the surface of ceramic fillers restrains their practical applications.

Recently, we designed a novel core@double-shells structured TiO\(_2\)@C@SiO\(_2\) NWs to simultaneously improve dielectric constant and suppress dielectric loss in the poly (vinylidene fluoride) (PVDF) matrix \([44]\). The carbon layer with a high electrical conductivity was chosen as the inner shell to provide strong polarization, while the SiO\(_2\) layer with an excellent insulated property was selected as the outer shell to act as a high resistivity barrier. However, it is still a challenge to efficiently regulate the dielectric performance to satisfy various application requirements of dielectric nanocomposites. Moreover, the influences of the conductive carbon inner shell and insulated SiO\(_2\) outer shell thicknesses on the dielectric performance have not been systematically investigated. In this work, the core@double-shells structured TiO\(_2\)@C@SiO\(_2\) NWs with variable carbon inner shell and SiO\(_2\) shell thickness was achieved by individually adjusting the CVD time and the amount of tetraethyl orthosilicate (TEOS) added in the sol-gel synthesis. The influence of each layer thickness on the dielectric performance of composites was systematically studied and the results showed that the proposed method could be an effective way to tailor the dielectric properties of the nanocomposites.

2 | EXPERIMENTAL

2.1 | Synthesis of core@double-shells structured TiO\(_2\)@C@SiO\(_2\) nanowires

The core@double-shells structured TiO\(_2\)@C@SiO\(_2\) nanowires were synthesised by a modified method with the combination of CVD and sol-gel synthesis as previously reported in our work \([44]\). The different carbon and SiO\(_2\) layer thicknesses were obtained by controlling over the CVD parameters and TEOS concentration, respectively.

Briefly, a certain amount of TiO\(_2\) nano-particle (Sigma-Aldrich) was homogeneously dissolved in 10 M NaOH (Sigma-Aldrich) aqueous solution and then the solution was transferred into a Teflon-autoclave followed by magnetically stirring at 200°C for 24 h. The obtained products were washed with deionised water for several times and then soaked in a diluted HCl aqueous solution with magnetically stirring for 4 h to obtain H\(_2\)Ti\(_3\)O\(_7\) NWs. After being washed with deionised water and then dried in an oven at 80°C overnight, the
resultant powders were further sintered at 600°C in air for 3 h in order to get TiO$_2$ NWs.

The carbon deposition on TiO$_2$ NWs was conducted by a CVD procedure at 850°C under argon (Ar) and hydrogen (H$_2$) atmosphere. The gas flow rate was 700 s.c.c.m. for Ar and 300 s.c.c.m. for H$_2$. After 5 min stabilisation, the carbon source C$_2$H$_2$ (40 s.c.c.m.) was introduced into the furnace. The deposition time was varied from 15 to 45 min in order to have different carbon layer thickness. For convenience and simplicity, the core-shell structured TiO$_2$@C NWs with different carbon shell thickness are denominated by TiO$_2$@C-\textit{X} NWs, where \textit{X} represents the carbon deposition time (min).

The SiO$_2$ layer was deposited on the previously obtained TiO$_2$@C NWs by a sol-gel method [45,46]. A stable TiO$_2$@C NWs suspension was obtained by dispersing the powders in 100 ml ethanol and 20 ml deionised water via 1 h ultrasonication. Then, a certain amount of TEOS was slowly injected into the above suspension and then the solution was ultrasonically treated for another 1 h. Then, 2 ml of ammonium hydroxide was dropwise added under a continuous magnetic stirring for another 4 h. Finally, the obtained powders were washed with ethanol several times until the solution pH is close to 7. The powders were subsequently dried in a vacuum oven at 75°C overnight. According to the TEOS volume (\textmu l) used, the TiO$_2$@C@SiO$_2$ NWs were denoted as TiO$_2$@C-\textit{Y} SiO$_2$ NWs, where \textit{Y} represents the TEOS volume.

2.2 | Nanocomposites fabrication

The three types of fillers (TiO$_2$ NWs, TiO$_2$@C NWs and TiO$_2$@C@SiO$_2$ NWs) were mixed into PVDF matrix by a solution casting way in order to fabricate the nanocomposites. First, a suspension containing the desired amount of fillers and N, N-dimethylformamide (DMF) was prepared through 2 h bath ultra-sonication. Next, PVDF powders (Kynar 761, Arkema) were dissolved into the homogeneously mixed suspension by using a magnetic stirrer. After 2 h stirring at 70°C, the DMF solvent was evaporated by increasing the temperature up to 100°C. Then, the resultant products were heat-treated at 80°C for 12 h in a vacuum oven. Finally, the PVDF nanocomposites incorporated with different fillers were obtained, in which the mass fraction of fillers varied from 0 to 30 wt.\%.

2.3 | Characterisations

Transmission electron microscopy (TEM) was used to study the coating microstructure and chemical composition of TiO$_2$@C NWs and TiO$_2$@C@SiO$_2$ NWs. A high-resolution TEM (FEI Titan Cube G2 60-300) equipped with a high-angle annular dark-field (HAADF) detector and an aberration-corrected condenser was operated at 200 kV. The elemental mapping was done with a scanning TEM-energy dispersive X-ray spectroscopy (STEM-EDX). The crystallographic structure of three types of NWs was analysed by X-ray diffraction (XRD, Bruker D2 PHASER with X-Flash 430). Raman spectroscopy (Jobin Yvon Lab Ram) was also employed to study the carbon layer characteristics before and after being coated with SiO$_2$. The thermal stability and detailed carbon composition of the different fillers were analysed by thermogravimetric (TGA, NETZSCH STA 449 F3) heating from room temperature to 800°C at 5°C min$^{-1}$ with an N$_2$/O$_2$ (20/20 s.c.c.m.) gas flow. The distribution of the NWs in PVDF matrix was characterised by scanning electron microscopy (SEM, HITACHI SU8010) operated at 5.0 kV. The dielectric properties (constant and loss) of the different nanocomposites films were investigated with an impedance analyser (Solatron 1260). Before the measurement, the two sides of each sample were metallized by coating a thin layer of silver paste to decrease the contact resistance between the sample and the electrodes. All the measurements were done at room temperature.

3 | RESULTS AND DISCUSSIONS

3.1 | The morphology and composition of core@double-shells structured TiO$_2$@C@SiO$_2$ NWs with variable thickness of carbon inner shell and SiO$_2$ outer shell

The multistep synthesis procedure for the TiO$_2$@C@SiO$_2$ NWs hybrids has been reported in our previous work [44]. The conductive carbon layers with different thickness were directly deposited on the surface of TiO$_2$ core through the decomposition of C$_2$H$_2$ in a CVD furnace to produce the TiO$_2$@C NWs. Afterwards, the TiO$_2$@C NWs were used as the template to be coated with an insulated SiO$_2$ outer shell to yield the coaxial core@double-shells TiO$_2$@C@SiO$_2$ NWs. As illustrated in Figure 1, the thickness of carbon inner shell and SiO$_2$ outer shell could be precisely regulated by controlling the CVD deposition time and the amount of TEOS added in the sol-gel synthesis process, respectively. Two series of TiO$_2$@C@SiO$_2$ NWs were obtained.
NWs hybrids were synthesised to be used for investigating the individual influence of the thickness of carbon inner shell and SiO$_2$ outer shell on the dielectric performance of the nano-composites. The first series of hybrids is the TiO$_2$@C-X@SiO$_2$-300 NWs with different carbon inner shell thickness and a given SiO$_2$ outer shell thickness, where X represents the CVD time. The other one is TiO$_2$@C-30@SiO$_2$-Y NWs with different SiO$_2$ outer shell thickness and a given carbon inner shell thickness, where Y represents the amount of TEOS added in the sol-gel process.

As shown in Figure S1a–c, the core@shell structure of TiO$_2$@C NWs with different carbon thickness could be clearly observed from the HAADF-STEM images. The TiO$_2$ core is uniformly wrapped by the carbon shell and the thickness of carbon shell could be precisely adjusted from 7 to 20 nm by controlling the time involved during CVD deposition from 15 to 45 min (Figure 2a). The STEM-EDS (Figure S1e–g) further provides persuasively visual evidence to confirm the core@shell structure. After the CVD process, the obtained TiO$_2$@C NWs subsequently served as the template in the sol-gel synthesis process to fabricate the core@double-shells structured hybrids. As presented in Figure 3b–d, the shell thickness was enlarged after the sol-gel procedure compared with that of TiO$_2$@C NWs (Figure 3a). Besides, the shell thickness could also be accurately regulated by changing the amount of TEOS involved in the sol-gel synthesis. Similarly, the successful construction of SiO$_2$ outer shell was further verified by the STEM-EDS tool (Figure 3e–i). The signal of Si element (Figure 3i) displays a stronger intensity in the shell compared with that in the core part and the signal of O element exhibits a hollow structure due to the lack of O element in the carbon inner shell. According to the enlargement of the shell thickness after the sol-gel synthesis, the thickness of SiO$_2$ outer shell could be calculated, and the calculation results (Figure 4) shows that its thickness could also be precisely controlled from 10 to 25 nm by adjusting the amount of TEOS involved in the sol-gel synthesis from 100 to 300 µl. According to these experimental results, the TiO$_2$@C@SiO$_2$ NWs hybrids with different carbon inner shell thickness and a given SiO$_2$ outer shell thickness (25 nm) were also prepared, as shown in Figure 2.

To obtain the accurate composition information about TiO$_2$@C and TiO$_2$@C@SiO$_2$ NWs hybrids, TGA characterisations were carried out as displayed in Figure 5a–c. The diffraction peaks from XRD patterns (Figure S2a) could be ascribed to the TiO$_2$ without any impurity according to JCPDS card No. 21-1272 [47]. After wrapped with the first carbon shell, the intensity of corresponding diffraction peaks of TiO$_2$ was weakened. The Raman spectroscopy (Figure S2b) confirms the existence of carbon shell, which exhibits two typical peaks with D band and G band. The intensity of corresponding diffraction peaks was further weakened after constructing the SiO$_2$ shell. However, due to the amorphous state of SiO$_2$, no obvious diffraction peak was observed from Figure S2a. Additionally, no significant band shift of D and G bands was detected after constructing the SiO$_2$ shell, which indicates that the SiO$_2$ and carbon shell is interacted by the non-covalent bond [45]. The TGA results of TiO$_2$@C NWs (Figure 5a and (d, i)) further verify the carbon content could be regulated from 11.64% to 24.72% by adjusting the CVD time from 15 to 45 min. As indicated in Figure 5(b), the carbon decomposition temperature increase from ca. 450 to 500°C after coating the TiO$_2$@C-30 NWs with SiO$_2$ outer shell, which could be

**Figure 2** HAADF-STEM images of the TiO$_2$@C-X@SiO$_2$-300 NWs with different carbon inner shell thickness

**Figure 3** HAADF-STEM images of the (a) TiO$_2$@C-30 NWs and (b)–(d) TiO$_2$@C-30@SiO$_2$-Y NWs with different SiO$_2$ outer shell thickness; (e) Enlarged HAADF-STEM image of TiO$_2$@C-30@SiO$_2$-300 NWs and corresponding (f)–(i) STEM-EDS element maps of Ti, O, C and Si, respectively.
ascribed to the blocking effect of SiO$_2$ outer shell. Besides, the monotonous decreasing of carbon content in TiO$_2$@C-30@SiO$_2$ NWs from 21.96% to 14.75% confirms that the carbon content could be controlled by changing the amount of TEOS in the sol-gel process (Figure 5(b) and (d, ii)), which reflects that the SiO$_2$ content could also be regulated. The evolution of carbon content for the TiO$_2$@C@SiO$_2$-300 NWs with the CVD time exhibits the similar law to that of TiO$_2$@C NWs (Figure 5(c) and 5(d, i)). The evolution law of carbon content with the CVD time and the amount of TEOS, obtained from the TGA curves, suggests that the carbon inner shell thickness and SiO$_2$ outer shell thickness could be precisely regulated by adjusting the experimental parameters involved in the CVD and sol-gel synthesis. As for the interfacial adhesion between NWs and PVDF matrix, the SEM images for the fractured surfaces of nanocomposites indicate that the interfacial adhesion could be strengthened by coating the TiO$_2$ core with the carbon and SiO$_2$ shells (Figure S3(b) and (c)). Even for the core@double-shells hybrids filled nanocomposite with 30 wt.% filler loading, the fillers disperse homogeneously in the PVDF matrix and their interfacial adhesion is strong (Figure S3(d)).

**FIGURE 4** The evolution of (a) carbon inner shell and (b) SiO$_2$ outer shell thickness on the experimental parameters during CVD deposition and sol-gel synthesis procedures.

**FIGURE 5** TGA curves of (a) TiO$_2$@C NWs with different carbon shell thickness, (b) TiO$_2$@C-30@SiO$_2$ NWs with different SiO$_2$ outer shell thickness, and (c) TiO$_2$@C@SiO$_2$-300 NWs with different carbon inner shell thickness; (d) the evolution of carbon weight loss calculated from TGA curves on the experimental parameters during CVD deposition and sol-gel synthesis procedures.
3.2 The influence of SiO$_2$ outer shell thickness on the dielectric performance of PVDF nanocomposites

As shown in Figures 6 and 8(a), (b), S4(a)–(c), the dielectric constants and losses of PVDF nanocomposites filled with different type of fillers all show a similarly gradual increase as the filler loadings increases. The dielectric constant of PVDF nanocomposites with TiO$_2$ NWs at $10^3$ Hz increases slightly from 9 to 20 with increasing the filler loading to 30 wt.% and the corresponding dielectric loss increases from 0.01 to 0.15. Compared with the dielectric constant of TiO$_2$ NWs filled nanocomposites, the constant of nanocomposites with TiO$_2$@C NWs exhibits a sharp increase as the filler loading increases to a certain value after coating the TiO$_2$ NWs core with a carbon shell (Figure S5(a)), which is a typical percolative behaviour for the nanocomposites with the conductive fillers [48]. However, the dramatic increase of dielectric constant is always accompanied by the sudden increase in dielectric loss (Figure S5(b)), which restricts their application in the electrostatic capacitors. Besides, the dielectric properties of nanocomposites with TiO$_2$@C NWs could be accurately regulated by controlling the carbon shell thickness. As shown in Figure S4(d), both the dielectric constant and loss of the nanocomposites with different types of TiO$_2$@C NWs increase with increasing the carbon shell thickness at the same filler loading, which is in accordance with the results reported in our previous work [9].

After coating the TiO$_2$@C NWs with the SiO$_2$ shell, both the dielectric constant and loss of TiO$_2$@C@SiO$_2$ NWs filled nanocomposites are significantly suppressed compared with those of nanocomposites with TiO$_2$@C NWs (Figure S5). Besides, the percolation phenomenon doesn’t occur even when the nanocomposites are incorporated with a high filler loading (30 wt.%) of TiO$_2$@C@SiO$_2$ NWs, which clearly reflects that the direct contact for the adjacent TiO$_2$@C NWs is efficiently prevented by the insulated SiO$_2$ outer shell. Moreover, it is worthy to note that the dielectric constant of the nanocomposites with core@double-shells structured TiO$_2$@C@SiO$_2$ NWs are largely enhanced after successively coating the TiO$_2$ NWs core with the carbon inner shell and SiO$_2$ outer shell when compared with that of TiO$_2$ NWs filled nanocomposites (Figure 7a). More importantly, the dielectric losses of the nanocomposites with core@double-shells structured NWs are simultaneously suppressed. The largely improved dielectric constant could be ascribed to the enhanced interfacial polarisations. For the TiO$_2$ NWs filled nanocomposites, only one type of interfacial polarization (TiO$_2$/PVDF interfacial polarization) exists in the nanocomposites. However, another two types of interfacial polarization ([1] TiO$_2$/carbon and [2] carbon/SiO$_2$ interfacial polarization) are additionally introduced into the
nanocomposites after successively coating the TiO$_2$ NWs core with the carbon inner shell and SiO$_2$ outer shell, which leads to a largely improved dielectric constant. As to the dielectric loss part, the largely suppressed loss could be attributed to the uniform layered structure and excellent insulated property of SiO$_2$ shell. In recent years, many researchers focussed their attention on either coating the ceramic fillers with the conductive shell to promote the dielectric constant or coating the conductive or high-$k$ fillers with the insulated shell to suppress the loss. This simple core@one-shell strategy reported could not simultaneously promote the constant and suppress the loss. The enhanced dielectric constant is always accompanied by the undesirable increase in dielectric loss. The simultaneous improvement of dielectric constant and restriction of dielectric loss is achieved here by this all-inorganic core@double-shells structured strategy. The carbon inner shell with high electrical conductivity is supposed to act as the polarisable domain, while the SiO$_2$ outer shell with a large resistivity is supposed to suppress the leakage current and dielectric loss as neighbouring particles contact with each other.

Besides, the dielectric properties of core@double-shells structured TiO$_2$@C@SiO$_2$ NWs filled PVDF nanocomposites could be precisely regulated by adjusting the carbon inner shell and SiO$_2$ outer shell thickness. As presented in Figure 7a, the dielectric constant of the TiO$_2$@C-30@SiO$_2$ NWs filled nanocomposites decreases with increasing the SiO$_2$ outer shell thickness at the same filler loading. For instance, the constant of the nanocomposites decreases from 50 to 41 at the same filler loading of 30 wt.% as the SiO$_2$ outer shell thickness increases from 10 to 25 nm. For the dielectric loss part, as given in Figure 7b, it exhibits the same tendency that the loss decreases with increasing the SiO$_2$ outer shell thickness. For example, the loss decreases from 0.13 to 0.05 at the same filler loading of 30 wt.% when the SiO$_2$ outer shell thickness increases from 10 to 25 nm. The frequency dependent behaviour of AC conductivity for the corresponding nanocomposites is given in Figure S6(a)–(c). For the TiO$_2$ NWs and TiO$_2$@C-30@SiO$_2$ NWs filled parts, their conductivity values exhibit a strong frequency-dependent behaviour in the whole frequency range, which reflects their insulating characteristic. However, the conductivity of TiO$_2$@C-30 NWs filled nanocomposites are almost independent of the frequency in the low-frequency range at the filler loading of 15 wt.%, which indicates that its conductive networks have been established due to the direct contact of the hybrids in the PVDF matrix. The SiO$_2$ outer shell thickness dependent behaviour of AC conductivities for TiO$_2$@C-30@SiO$_2$ NWs filled nanocomposites exhibits the same tendency to those of dielectric constant and loss parts, which would not be described in detail (Figure S6(f)).

### 3.3 The influence of carbon inner shell thickness on the dielectric performance of PVDF nanocomposites

The influence of carbon inner shell thickness on the dielectric constant and loss of the core@double-shells structured TiO$_2$@C@SiO$_2$ NWS filled PVDF nanocomposites is given in Figure 8. As shown in Figures 6(d) and 8(a), (b), the constant and loss of TiO$_2$@C@SiO$_2$-300 NWS filled PVDF nanocomposites increases slightly with increasing of filler loading. Compared with the dielectric performance of TiO$_2$ NWs filled PVDF nanocomposites, the dielectric constants and losses of the nanocomposites with TiO$_2$@C@SiO$_2$-300 NWs are simultaneously improved and suppressed, respectively (Figure 8(c) and (d)). Besides, the dielectric properties could also be precisely regulated by controlling the carbon inner shell thickness. As compared with the effect of SiO$_2$ outer shell on the dielectric performance, the influence of carbon inner shell exhibits a contrary tendency that both the dielectric constant and loss increase with the increasing of the
carbon inner shell thickness. For instance, the dielectric constant of the nanocomposites increases from 37 to 52 as the carbon inner shell thickness increases from 7 to 20 nm at the same filler loading of 30 wt.%. As for the dielectric loss, it increases from 0.04 to 0.08 with increasing the carbon inner shell thickness from 7 to 20 nm at the same filler loading of 30 wt.%. The evolution of the dielectric constant and loss of the nanocomposites with carbon inner shell thickness is similar to that of core@one-shell TiO$_2$@C NWs filled nanocomposites. The increasing of conductive carbon inner shell thickness enhances the interfacial polarization between the TiO$_2$ core and SiO$_2$ outer shell, which promotes the enhancement of the dielectric constant and loss. As shown in Figure S7, the effects of carbon inner shell thickness on the AC conductivity exhibits the similar tendency to that of dielectric constant and loss parts, which would not be discussed in details.

3.4 Insights from the computer simulation

As known, the current density was an important factor determining the dielectric loss of polymer nanocomposites. In order to theoretically explain the evolution of dielectric loss with the SiO$_2$ outer shell thickness, the simulation of the finite element was used to analyse the current density distribution in the polymer nanocomposites. As confirmed by the SEM images (Figure S3), most of the NWs in the PVDF matrix were aligned along the in-plane-oriented direction. The distribution of current density was simulated as illustrated in Figures 9 and S8. The contrast of local electric current density was mainly attributed to the local electric resistivity difference between fillers and polymer matrix. The simulated current densities of nanocomposites with pristine TiO$_2$ NWs and TiO$_2$@C NWs change more abruptly than that of nanocomposites with core@double-shells structured TiO$_2$@C@SiO$_2$ NWs with different SiO$_2$ outer shell thickness from top to bottom part (Figures 9 and S8). Moreover, the simulated current density changes more gradually with increasing the SiO$_2$ outer shell thickness (Figure 9(b)–(d)). Besides, the nanocomposites with core@double-shells hybrids exhibit the lowest current density compared with pristine TiO$_2$ NWs and TiO$_2$@C NWs filled ones. The excellent insulated property of SiO$_2$ outer shell afford the nanocomposites with the lowest current density by confining the mobility of free electrons and the percolated current from carbon inner shell. The absolute current density values also decrease with increasing the SiO$_2$ outer shell thickness (Figure 9(b)–(d)). The current density evolution law and the absolute current density values for the nanocomposites with different hybrids fillers all verify the accuracy and reliability.
of experimental results that the TiO$_2$@C@SiO$_2$ NWs filled nanocomposites own the lowest dielectric loss and the dielectric loss decrease with increasing the SiO$_2$ outer shell thickness.

4 | CONCLUSION

In conclusion, the controllable synthesis of core@double-shells structured NWs with variable shells thickness was realised by regulating the CVD time and amount of silicon precursor in the sol–gel synthesis process. All core@double-shells structured NWs filled nanocomposites exhibit an excellent dielectric performance with simultaneously improved dielectric constant and suppressed loss when compared with that of the TiO$_2$ NWs filled ones at the same filler loading. More importantly, the dielectric performance could be precisely regulated by individually changing the thickness of the conductive carbon inner shell and insulated SiO$_2$ outer shell. The influences of carbon inner shell and SiO$_2$ outer shell thickness on the dielectric performance of nanocomposites were systematically investigated. The dielectric constant and loss of nanocomposites increase with the increasing carbon inner shell thickness and decrease with the increasing SiO$_2$ outer shell thickness. The relationship between the dielectric loss and SiO$_2$ outer shell thickness was further demonstrated by the finite simulation results. The controllable core@double-shells structure reported here makes them a promising candidate to tailor the dielectric performance of advanced dielectric nanocomposites.

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