

**Largely Enhanced Dielectric Constant of PVDF Nanocomposites through a  
Core-Shell Strategy**

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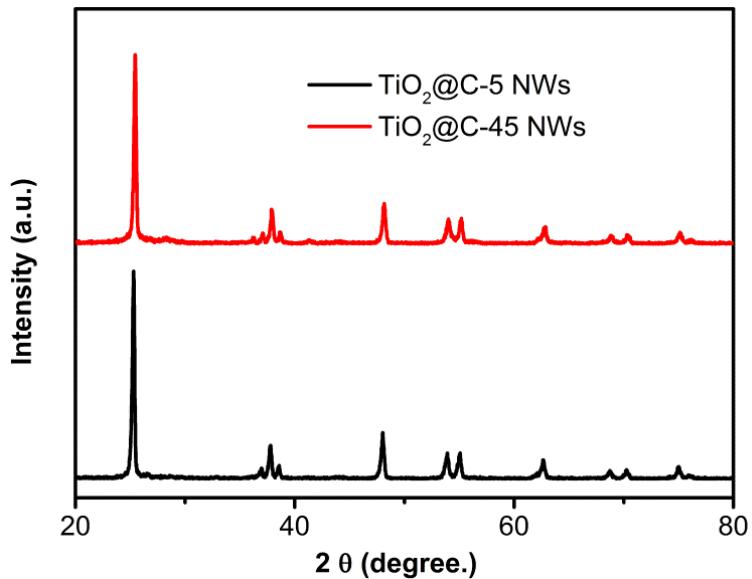
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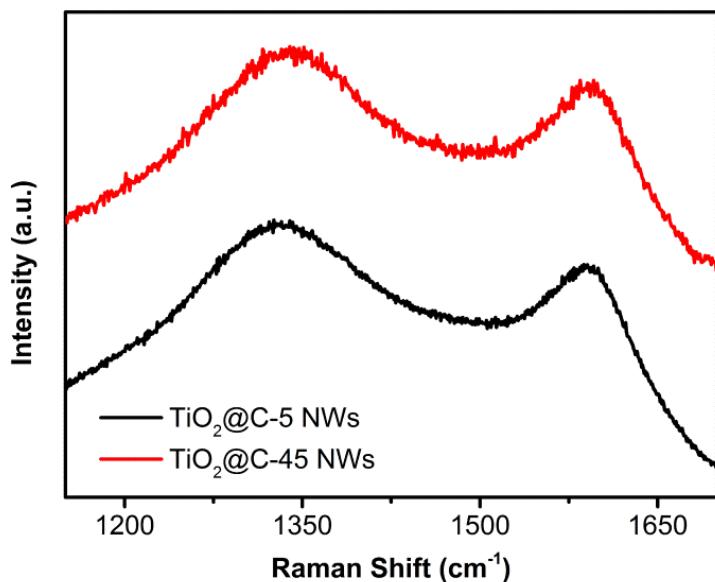
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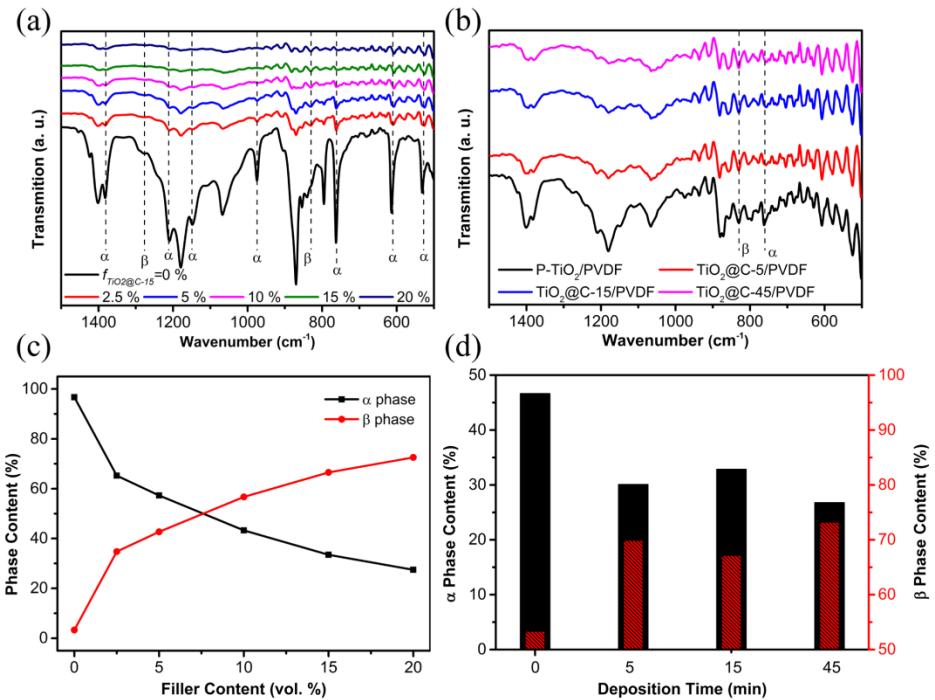
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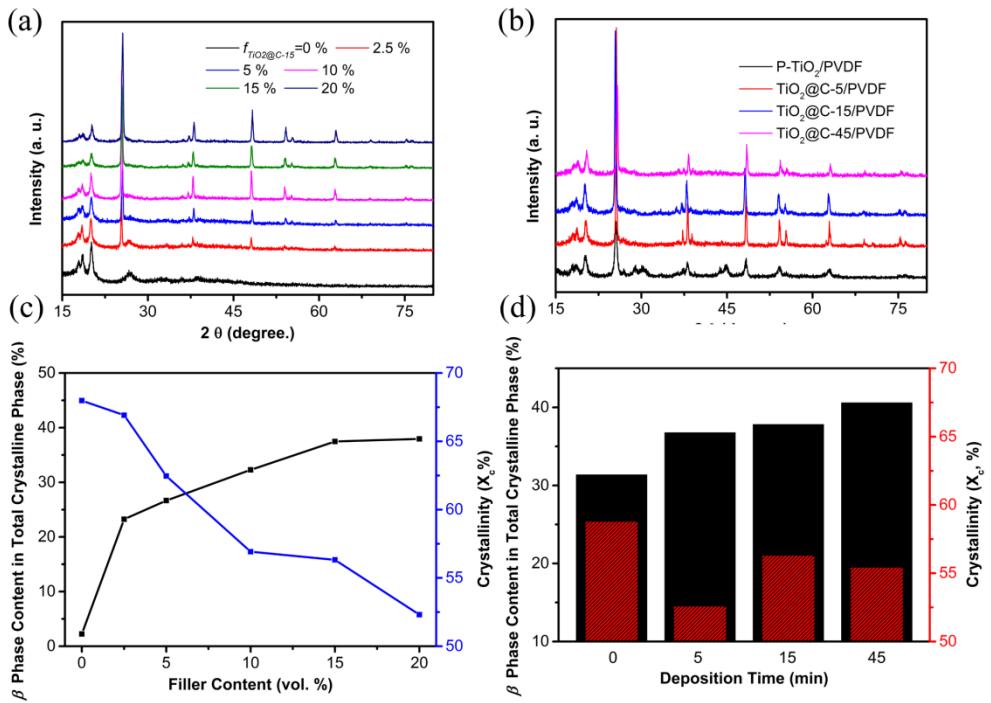
**Fig. S1** XRD patterns of  $\text{TiO}_2@\text{C}$  NWs hybrids with different carbon shell thickness.



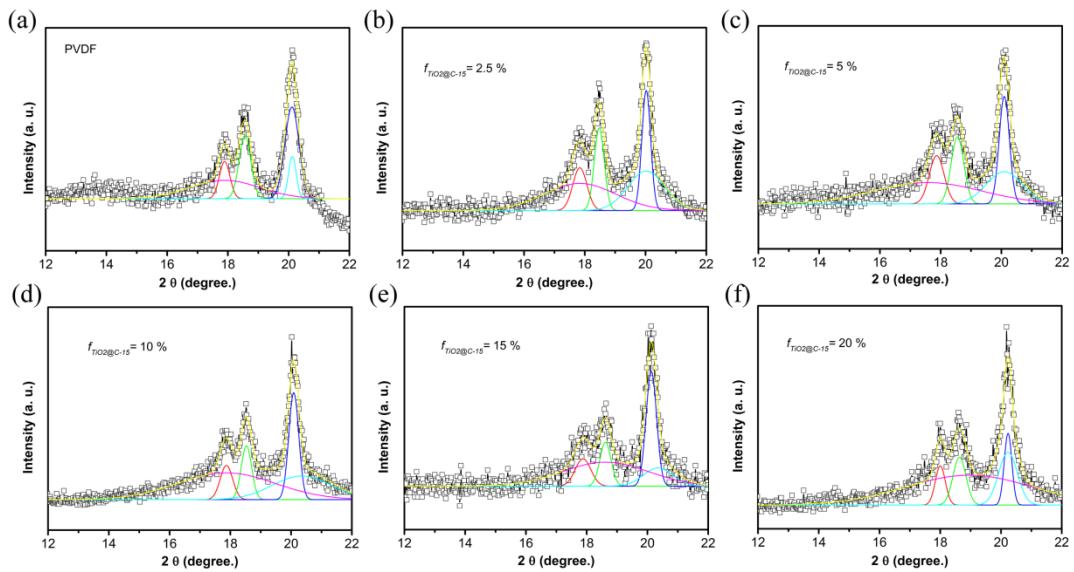
**Fig. S2** Raman spectra of  $\text{TiO}_2@\text{C}$  NWs hybrids with different carbon shell thickness.



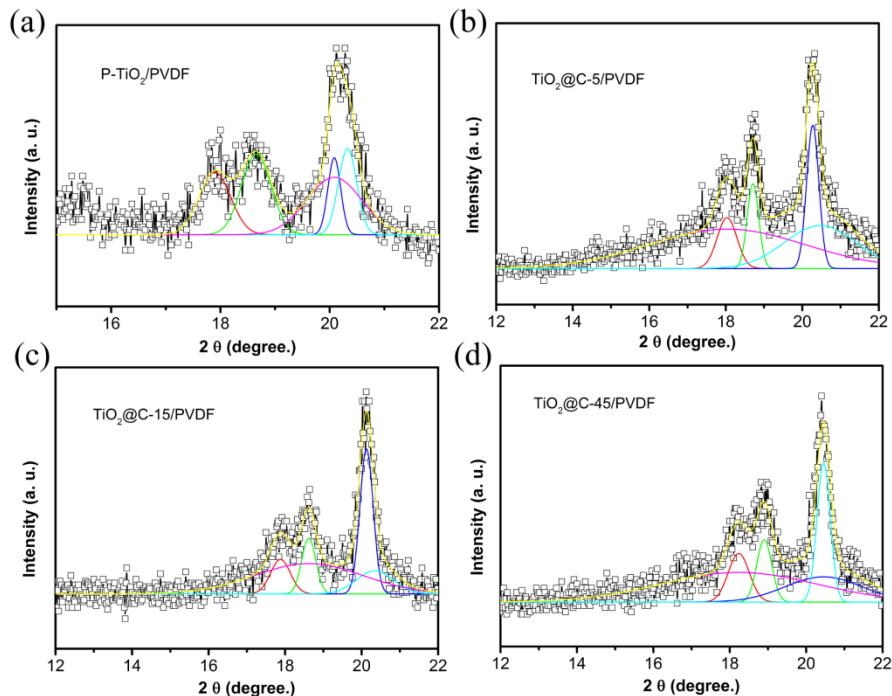
**Fig. S3** FT-IR spectra of (a) PVDF and TiO<sub>2</sub>@C-15 NWs/PVDF nanocomposites with different filler loadings and (b) TiO<sub>2</sub> NWs/PVDF and TiO<sub>2</sub>@C NWs/PVDF nanocomposites with different hybrids at the same filler loading (15 vol. %); (c) The calculated relative content of α and β phase in PVDF and TiO<sub>2</sub>@C-15 NWs/PVDF nanocomposites as a function of filler loading; (d) The calculated relative content of α and β phase in TiO<sub>2</sub> NWs/PVDF and TiO<sub>2</sub>@C NWs/PVDF nanocomposites at 15 vol. % filler loading as a function of CVD time.



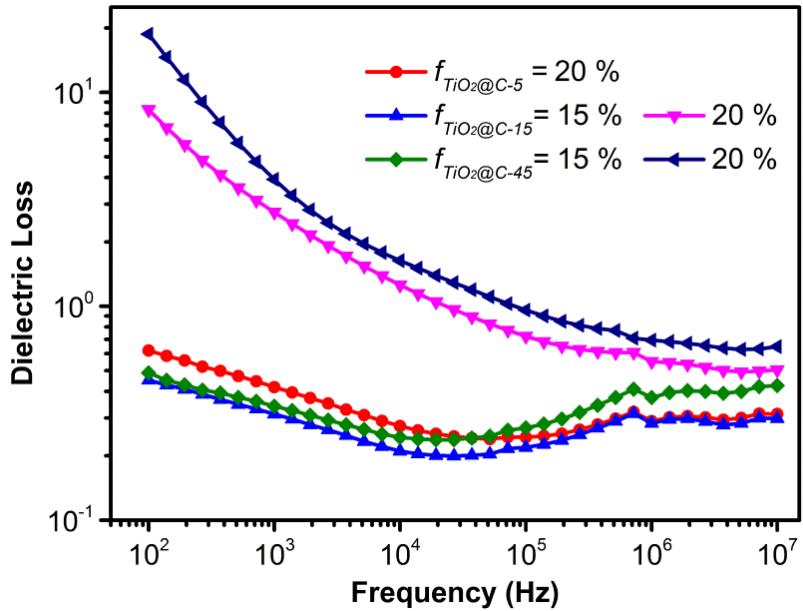
**Fig. S4** XRD patterns of (a) PVDF and TiO<sub>2</sub>@C-15 NWs/PVDF nanocomposites with different filler loadings and (b) TiO<sub>2</sub> NWs/PVDF and TiO<sub>2</sub>@C NWs/PVDF nanocomposites with different hybrids at the same filler loading (15 vol. %); (c) The calculated content of β phase in total crystalline phase of PVDF and TiO<sub>2</sub>@C-15 NWs/PVDF nanocomposites as a function of filler loading; (d) The calculated content of β phase in total crystalline phase of TiO<sub>2</sub> NWs/PVDF and TiO<sub>2</sub>@C NWs/PVDF nanocomposites at 15 vol. % filler loading as a function of CVD time.



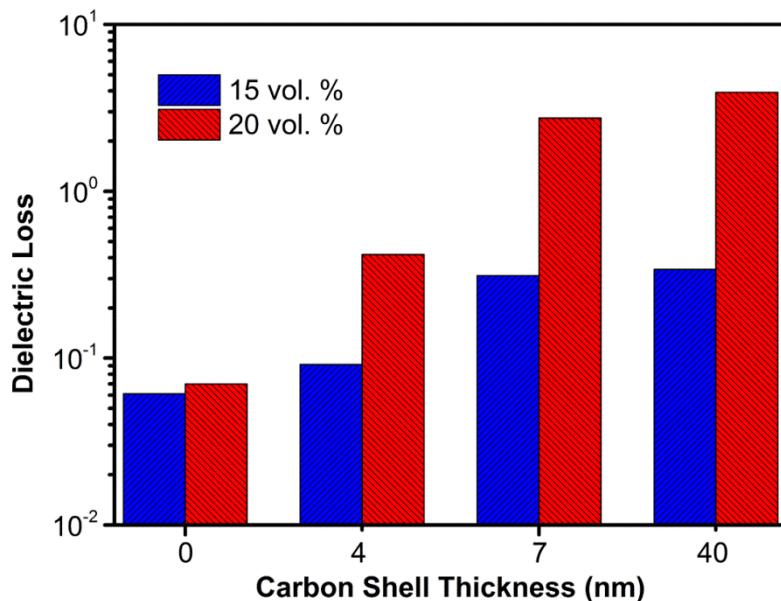
**Fig. S5** Origin's multiple peak separation fitting results of PVDF and TiO<sub>2</sub>@C-15 NWs/PVDF nanocomposites with different filler loadings.



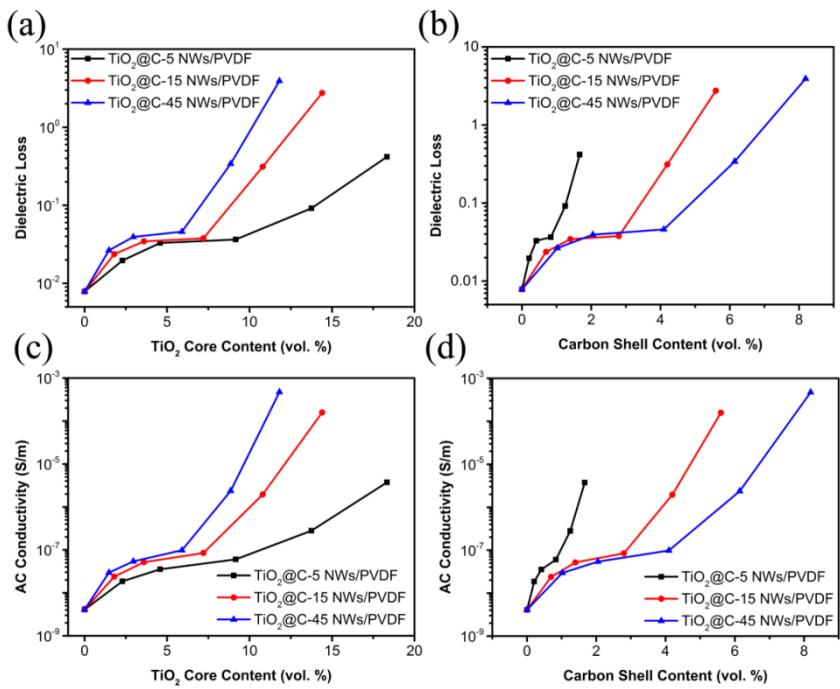
**Fig. S6** Origin's multiple peak separation fitting results of TiO<sub>2</sub> NWs/PVDF and TiO<sub>2</sub>@C NWs/PVDF nanocomposites with different hybrids at the same filler loading (15 vol. %).



**Fig. S7** Frequency dependence of the dielectric loss values of  $TiO_2@C-5$  NWs/PVDF,  $TiO_2@C-15$  NWs/PVDF and  $TiO_2@C-45$  NWs/PVDF nanocomposites at different filler loadings.

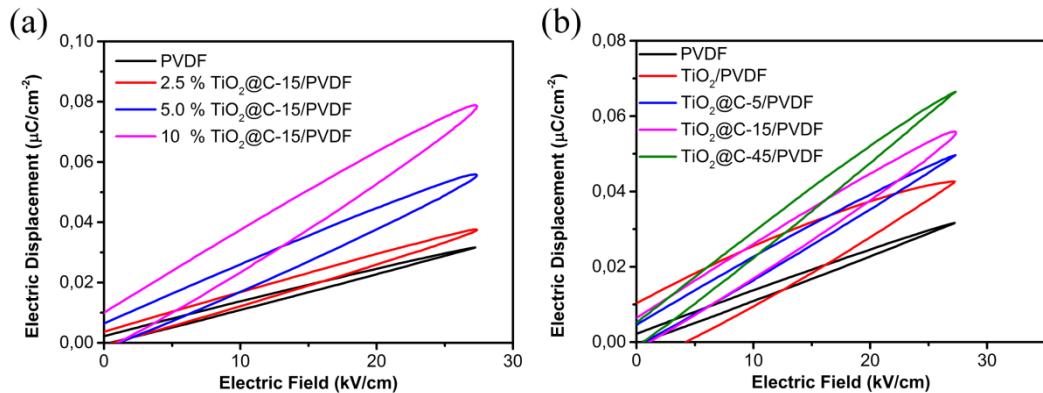


**Fig. S8** Typical variation of dielectric loss values ( $10^3$  Hz) of  $TiO_2$  NWs/PVDF,  $TiO_2@C-5$  NWs/PVDF,  $TiO_2@C-15$  NWs/PVDF, and  $TiO_2@C-45$  NWs/PVDF nanocomposites as a function of carbon shell thickness at different filler loadings ( 15 vol. % and 20 vol. %).



**Fig. S9** Dependence of the dielectric loss and AC conductivity of TiO<sub>2</sub>@C-5

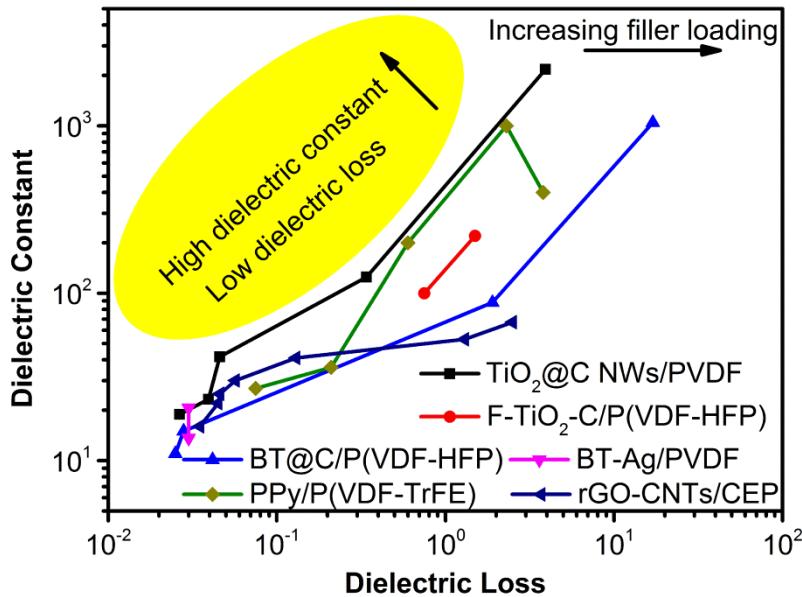
NWs/PVDF, TiO<sub>2</sub>@C-15 NWs/PVDF, and TiO<sub>2</sub>@C-45 NWs/PVDF nanocomposites on the volume fraction of the TiO<sub>2</sub> NWs core and carbon shell for the whole nanocomposites (10<sup>3</sup> Hz).



**Fig. S10** The D-E loops of (a) PVDF and TiO<sub>2</sub>@C-15 NWs/PVDF nanocomposites

with different filler loadings (b) TiO<sub>2</sub> NWs/PVDF and TiO<sub>2</sub>@C NWs/PVDF

nanocomposites with different hybrids at the same filler loading (5 vol. %) at 10 Hz.



**Fig. S11** Comparison of dielectric properties ( $10^3$  Hz) of percolative nanocomposites

with different types of nano-filters: **TiO<sub>2</sub>@C NWs**, 2.5-20 vol. %; **Flower-like TiO<sub>2</sub>-C**, 15 and 20 vol. %; **BT@C**, 5-30 vol. %; **BT-Ag**, 7.6 and 18 vol. %; **PPy nanoclips**, 3-9 wt. %; **rGO-CNTs**, 0.02-0.144 wt. % [1, 2, 3, 4, 5].

#### The derivation process of volume fraction of carbon shell ( $\alpha$ ):

The volume fraction of carbon shell in the hybrids ( $\alpha$ ) could be calculated from the weight fraction of carbon shell ( $\beta$ ) as described below. The weight fraction of carbon shell in the hybrids could be obtained from the TGA curves. The equation for the calculation of  $\alpha$  could be expressed as below.

$$\alpha = \frac{V_c}{V_h} = \frac{V_c}{V_c + V_{TiO_2}} = \frac{\beta M / \rho_c}{\beta M / \rho_c + (1 - \beta)M / \rho_{TiO_2}} = \frac{\beta / \rho_c}{\beta / \rho_c + (1 - \beta) / \rho_{TiO_2}}$$

where  $V_c$ ,  $V_{TiO_2}$ , and  $V_h$  are the volume of carbon shell, TiO<sub>2</sub> core, and hybrids, respectively. The  $\rho_c$  and  $\rho_{TiO_2}$  represent the density of carbon shell and TiO<sub>2</sub> core, respectively, and  $M$  is the mass of hybrids. The  $\rho_c$  and  $\rho_{TiO_2}$  values are selected as 2.00 g cm<sup>-3</sup> and 3.90 g cm<sup>-3</sup>, respectively. The  $\beta$  is directly extracted from the TGA results.

Then the corresponding numerical values are put into the above-mentioned equation, and then the corresponding  $\alpha$  could be obtained. The  $\alpha$  for the TiO<sub>2</sub>@C-5 NWs, TiO<sub>2</sub>@C-15 NWs, and TiO<sub>2</sub>@C-45 NWs are 8.34 %, 27.99 %, and 40.95 %, respectively.

1 L. Zhang, Z. Liu, X. Lu, G. Yang, X. Zhang and Z. Y. Cheng, *Nano Energy*, 2016, **26**, 550-557.

2 S. Luo, S. Yu, R. Sun and C. P. Wong, *ACS Appl. Mater. Interfaces*, 2013, **6**, 176-182.

3 Y. Feng, W. Li, J. Wang, J. Yin and W. Fei, *J. Mater. Chem. A.*, 2015, **3**, 20313-20321.

4 N. Xu, Q. Zhang, H. Yang, Y. Xia and Y. Jiang, *Sci. Rep.*, 2017, **7**, 43970.

5 J. Y. Kim, T. Kim, J. W. Suk, H. Chou, J. H. Jang, J. H. Lee, I. N. Kholmanov, D. Akinwande and R. S. Ruoff, *Small*, 2014, **10**, 3405-3411.