Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A Facile One-Step Grafting of Polyphosphonium onto Halloysite Nanotubes Initiated by Ce(IV)

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1. Experimental Procedures

1.1 Materials

HNTs were obtained from GuangZhouShinshi Metallurgy and Chemical Company Ltd (Guangzhou, China) and purified according to our previous work [1]. Triethylphosphine and 1-(chloromethyl)-4-ethenyl-benzen were purchased from Sigma-Aldrich. Aluminum oxide nanometer (30 nm), silica nanospheres (50 nm) and sodium alginate were purchased from J&K Chemical Technology. Ammonium cerium(IV) nitrate (CAN) was purchased from Kemiou Chemical Reagent Co., Ltd. Dimethyl sulfoxide (DMSO) was dried and distilled from CaH_2 under vacuum before use. Distilled water was used throughout the study. High-purity argon was used for degassing procedures. Triethyl(4-vinylbenzyl)phosphonium chloride (Et-P) was synthesized according to the literature [2].

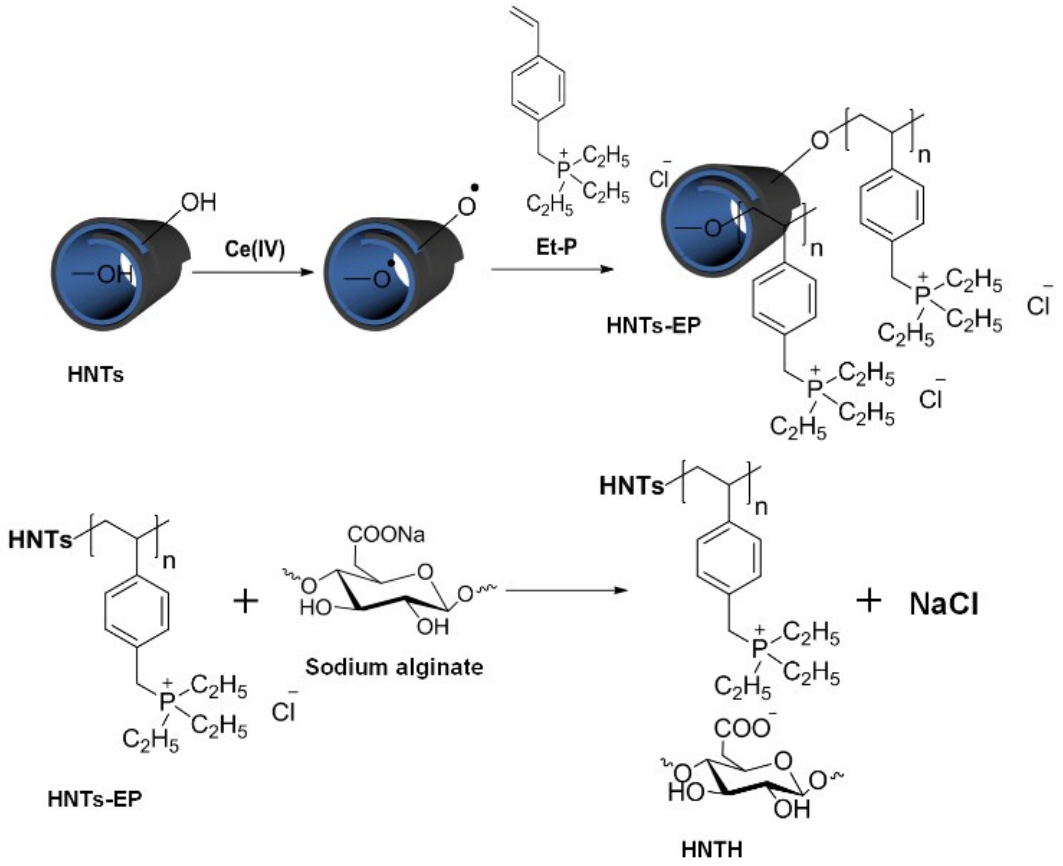
1.2 Preparations

1.2.1 Preparation of HNTs-EP

A mixture of purified HNTs (200 mg), Et-P (200 mg, 0.74 mmol) and CAN (30 mg, 0.13 mmol) in 3 mL water was carefully degassed and then stirred under nitrogen atmosphere at 35°C for 12 h. The mixture was cooled to ambient temperature and then washed triply and sequentially by DMSO and dichloromethane. The residue was extracted by Soxhlet extraction and then collected by centrifugation. After vacuum-drying, the HNTs-EP was obtained as a faint yellow solid.

1.2.2 Preparation of HNTs-based hydrogel (HNTH)

0.36 g sodium alginate was added into 20 mL 0.1 M NaCl solution and the pH value was adjusted to 8.0 with the addition of NaOH to give the sodium alginate solution. 120 mg HNTs-EP was dispersed into 0.2 mL 0.1 M NaCl solution followed by 1.5 mL sodium alginate solution was added dropwise. Then the residue was collected by centrifugation at 8000 rpm and then added into 0.25 M NaCl solution. The system was heated at 50 ^{o}C for 3 h to give the product HNTH.



Scheme 1. Preparation of poly(Et-P) grafted HNTs (HNTs-EP) and the HNTs-based hydrogel (HNTH).

1.3 Characterizations

The morphological characterizations were performed by using a Tecnai G2 F20 S-TWIN transmission electron microscope (TEM) with an accelerating voltage of 200 kV. A JEOL Ltd. JSM-7500F Cryo field emission scanning electron microscopy (SEM) was also used to characterize the micromorphology of prepared hydrogels. The fluffy samples were carefully put on flat substrates precoated with carbonic glues and then were coated with gold for SEM observations. FTIR spectra were recorded in the region of 400-4000 cm^{-1} for each sample on a Varian-640 spectrophotometer. Samples were previously ground and mixed thoroughly with KBr. The ^{13}C Solid-state NMR spectra were obtained on a Bruker Advance III spectrometer. ^{1}H NMR spectra were recorded on a Bruker AVANCE-600 600 MHz spectrometer (Bruker, Germany). The sample as dissolved in D_2O (δ = 4.79 in ^{1}H NMR spectrum). X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Scientific ESCALab 250Xi using 200 W

monochromated Al Ka radiation. The 500 μm X-ray spot was used for XPS analysis. The base pressure in the analysis chamber was about 3×10^{-10} mbar. Typically, the hydrocarbon C1s line at 284.8 eV from adventitious carbon was used for energy referencing. TGA was performed on Perkin-Elmer Pyris 6 at a scanning rate of 10 ^{o}C/min from 40 to 800 ^{o}C under nitrogen. UV-visible absorption spectra were obtained on a Shimadzu UV-visible spectrometer model UV-2550. The optical densities of the bacteria at 600 nm were measured using a TU-1901 ultraviolet-visible spectrophotometer (Purkinje, China) and a microplate reader SpectraMax M2 (Molecular Devices). Plate counting photographs were taken by a VersaDoc imaging system (Bio-RAD)

1.4 Bacterial Culture

Kana^{r} Gram-negative *E. coli* (BL21) was used as the test model. Firstly, Kana^{r} BL21 picked from a single colony was transferred to 10 mL of the Luria-Bertani (LB) and then incubated in darkness to achieve a density of 0.5 at 600 nm (OD_{600} = 0.5). The rotation speed was set as 180 rpm, the temperature was 37 ^{o}C, and the incubation time was about 4 h. Afterwards, the bacterial solution was centrifugated at 8000 rpm for 2 min and the supernatant was carefully removed. The residual bacterial solutions were wash with phosphate-buffered saline buffer (1×) for twice and suspended in it.

1.5 Antibacterial test

Aliquot of 500 μL of the kanar Gram-negative *E. coli* solution (OD_{600} = 0.5) was transferred into a 24-well plate, in each well of which were added HNTs suspension, HNTH suspension and sodium alginate solution, to a final volume of 1.0 mL. The above three kanar Gram-negative *E. coli* solutions in the 24-well plate, accompanying with a solution contained kanar Gram-negative *E. coli* only, were cultured for 2 h in darkness at 37 °C and rotation speed was also set as 180 rpm. Afterwards, the solutions were transferred to 1.5 mL centrifuge tubes and centrifugated at 8000 rpm, respectively, for 2 min and then were washed with PBS buffer. After removing the supernatant, all of the remaining kanar Gram-negative *E. coli* were resuspended in PBS buffer and serially diluted 1×10^{4} fold with PBS, respectively. Subsequently, a 100 μL portion of the bacterial dilution was spread on the solid LB agar plate and the colonies formed after

12 h incubation at 37 °C in the dark were counted. Each group of samples was performed through three parallel experiments. The killing efficiency (%) was calculated according to the following equation:

$$\text{Killing Efficiency (\%)} = (S_0\text{-}S)/S_0 \times 100\% \quad (1)$$

where S is the colony forming units (CFU) of the experimental group treated with HNTs, HNTH and sodium alginate, respectively, and S_0 is the CFU of the kanar Gram-negative *E. coli* only, without any treatment.

1.6 Stability test of HNTs-EP

The stability of prepared HNTs-EP was evaluated by treating HNTs-EP for 10 h at 25 °C. The residue was collected by centrifuged at 8000 rpm and then freeze-dried to give the test sample.

1.7 Model experiment of Al_2O_3 and SiO_2 nanoparticles

A mixture of Al_2O_3 or SiO_2 nanoparticles (200 mg), Et-P (200 mg, 0.74 mmol) and CAN (30 mg, 0.13 mmol) in 3 mL water was carefully degassed and then stirred under nitrogen atmosphere at 35°C for 12 h. The mixture was cooled to ambient temperature and then washed triply and sequentially by DMSO and dichloromethane. The residue was extracted by Soxhlet extraction and then collected by centrifugation. The Et-P treated Al_2O_3 or SiO_2 nanoparticles were afforded after vacuum-drying.

2. FTIR, NMR, TEM, XPS and GPC Data

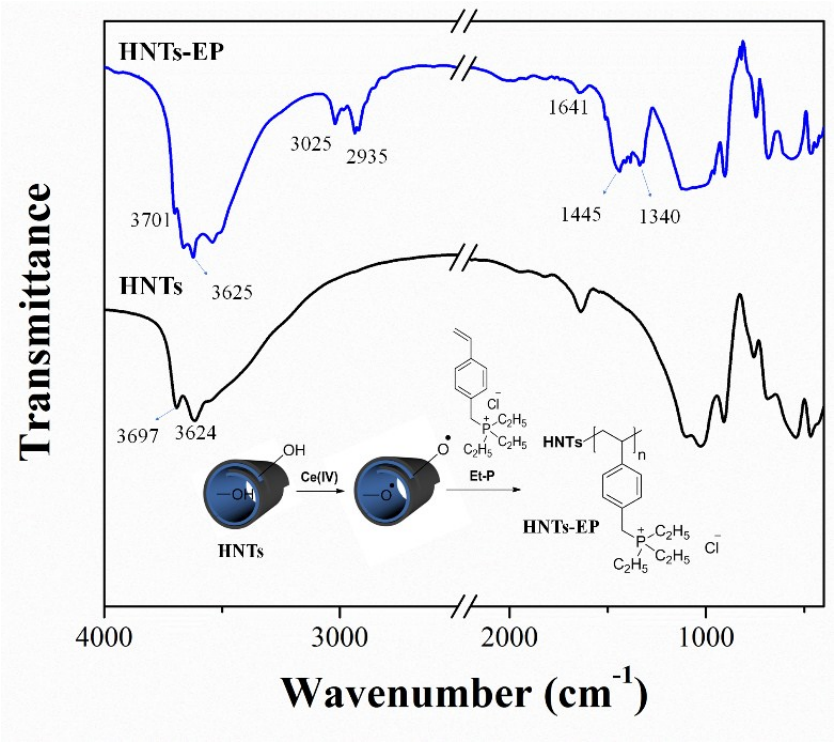


Figure S1. FT-IR spectra of HNTs and HNTs-EP and the proposed initiation mechanism

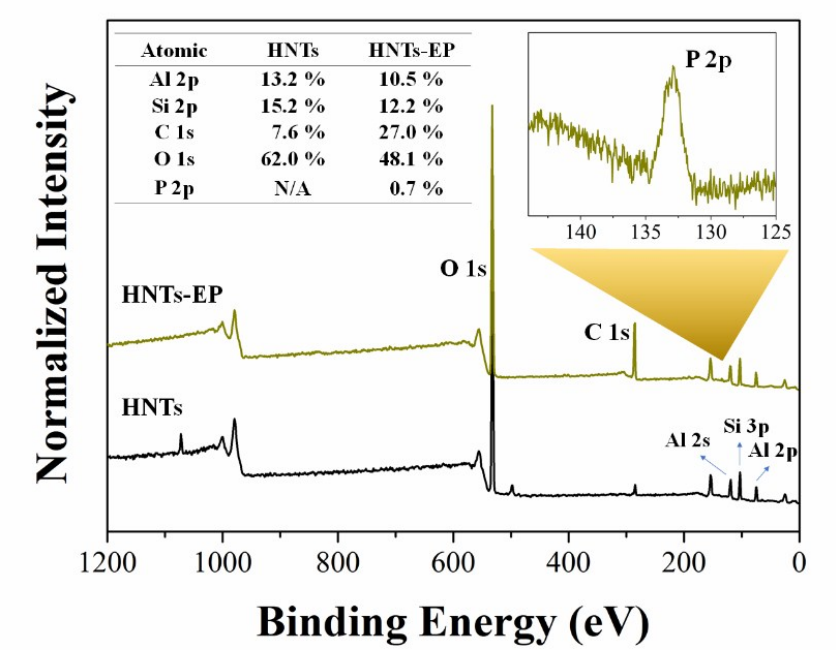


Figure S2. XPS spectra of HNTs and HNTs-EP

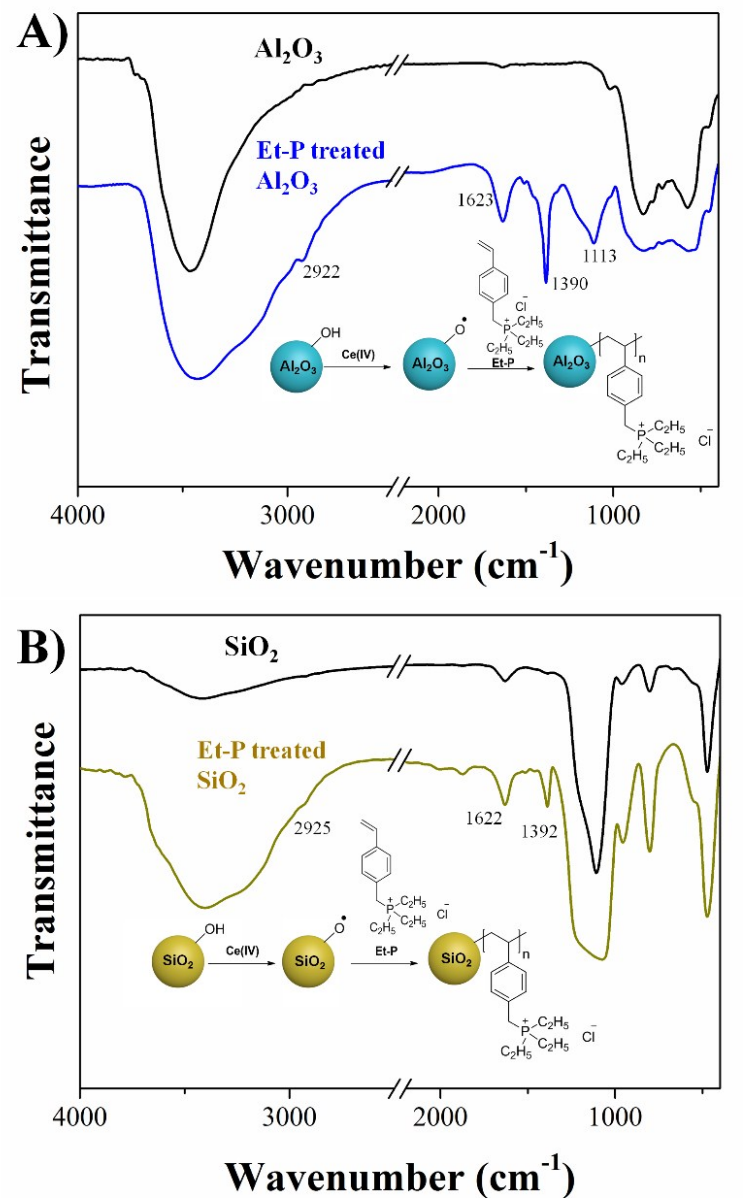


Figure S3. FT-IR spectra of (A) Al_2O_3 and (B) SiO_2 nanoparticles before and after Et-P treatment.

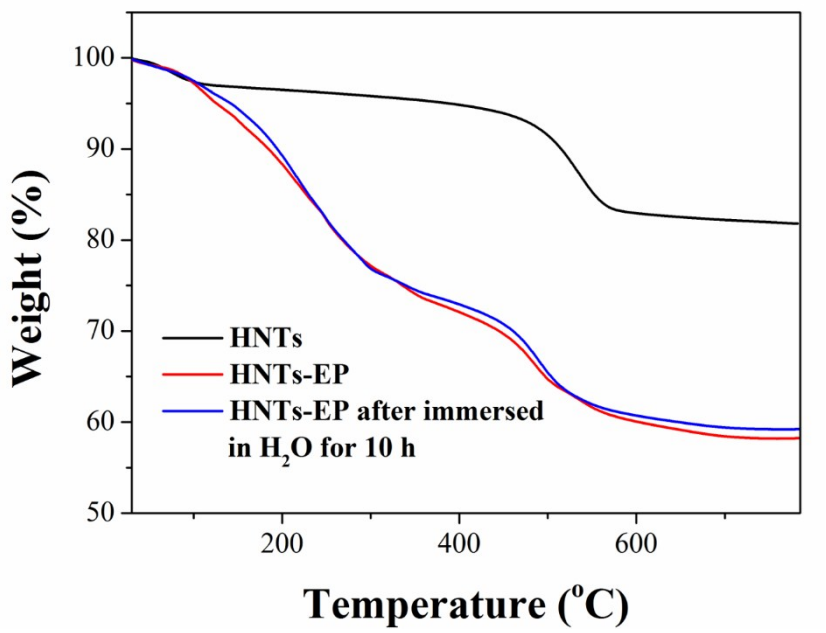


Figure S4. TGA curves of HNTs, HNTs-EP and HNTs-EP after immersed in H_2O for 10 h.

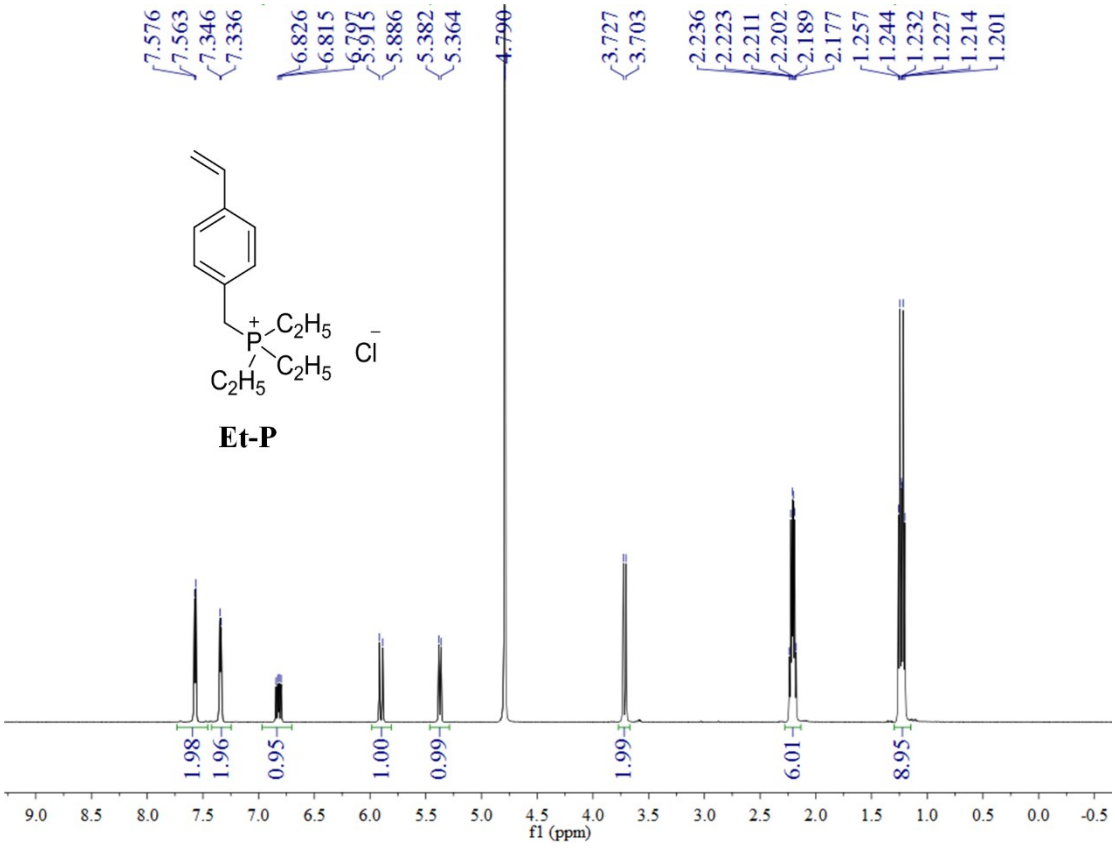


Figure S5. ^1H NMR spectrum of triethyl(4-vinylbenzyl)phosphonium chloride (Et-P).

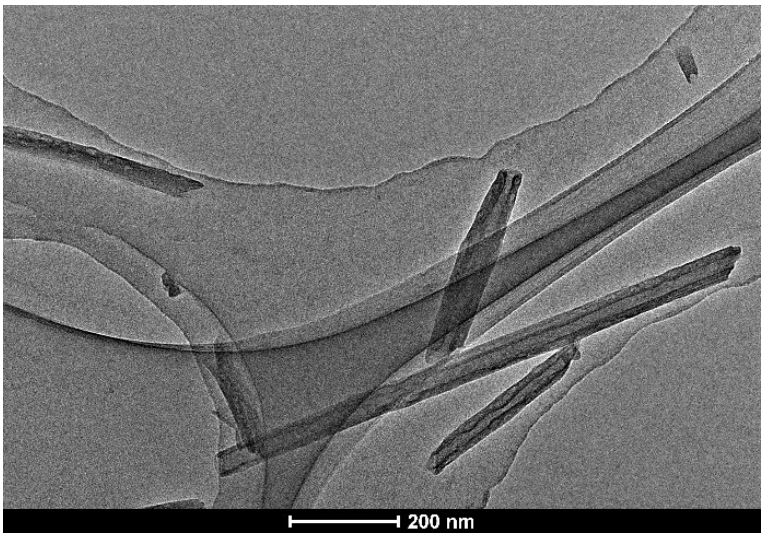


Figure S6. Some unexpected damage occurred on the nanotubes when the Ce(IV) concentration is higher than 10 mg/mL.

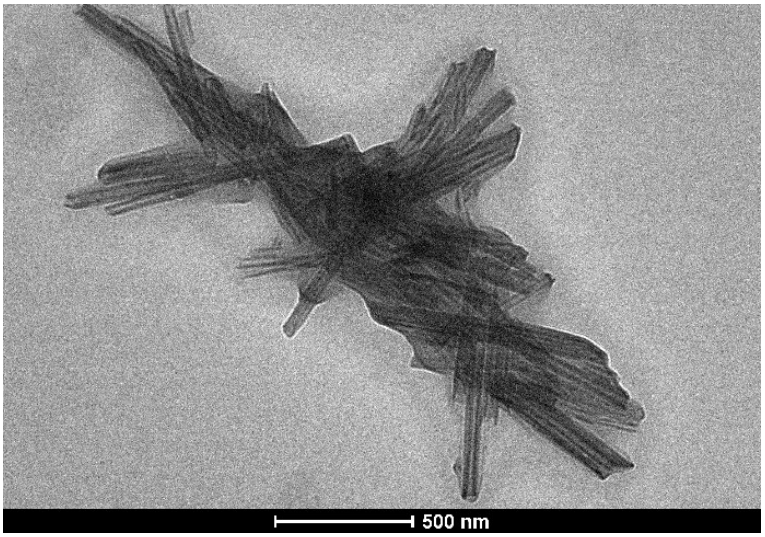


Figure S7. Some unexpected aggregation occurred when the addition amount of Et-P is higher than 200 mg.

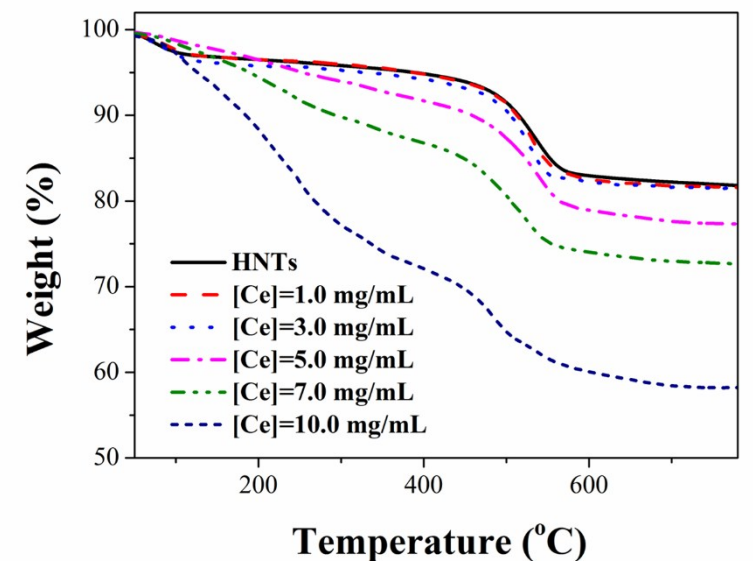


Figure S8. TG curves of the HNT-polyphosphonium products (HNTs-EP) prepared in different concentration of Ce(IV). (It is difficult to find any significant differences in the TG curves between HNTs and Ce(IV)-treated product when the concentration of Ce(IV) is 1.0 mg /mL or 3.0 mg /mL. The grafting degree increased from 6 to 29% as the increase of Ce(IV) concentration from 5.0 to 10.0 mg/mL. So, in our study, we prepared HNTs-EP by treating HNTs in 10.0 mg /mL solution in which little damage can be found in the product.)

Figure S9. The photo of an aqueous suspension containing poly (Et-P)-grafted HNTs (1 mg/mL) lasting for 24 h.

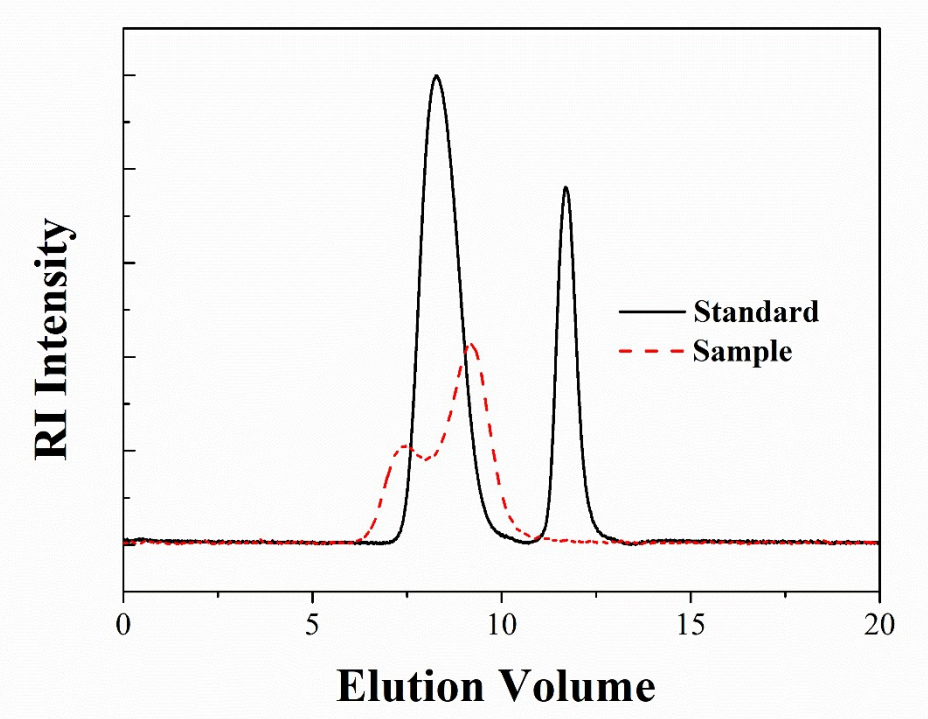


Figure S10. GPC curves of standard (M_p=2.75 × 10^4 g/mol, 5.9 × 10^3 g/mol) and polyphosphonium sample (the polyphosphonium sample was obtained by treating HNTs-EP in HF solution, M_w=2.35 × 10^4 g/mol): The molecular weight of the grafted polyphosphonium was measured by treating HNTs-EP with hydrofluoric acid. After centrifugation for the remove of the nanotubes, the polymers were obtained by precipitating the supernate into excess acetone. Then the molecular weight was determined by Viscotek 270-doul detector-Size Exclusion Chromatography which equipped with differential refractive index (RI) by using polyoxyethylene as standard. The weight-average molecular weight of grafted polyphosphonium on HNTs-EP was calculated as 2.35 × 10^4 g/mol.

Reference

1. a) H. Zhang, T. Ren, Y. Ji, L. Han, Y. Wu, H. Song, L. Bai and X. Ba, *ACS Appl. Mater. Interfaces*, 2015, **7**, 23805-23811; b) H. Zhang, X. Zhu, Y. Wu, H. Song and X. Ba, *J. Mater. Sci.*, 2015, **50**, 4387-4395; c) F. Liu, L. Bai, H. Zhang, H. Song, L. Hu, Y. Wu and X. Ba, *ACS Appl. Mater. Interfaces*, 2017, **9**, 31626-31633.
2. T. J. Cuthbert, T. D. Harrison, P. J. Ragogna and E. R. Gillies, *J. Mater. Chem. B*, 2016, **4**, 4872-4883.