Experimental

Preparation of hollow CaP nanospheres: A known amount of PS-*b*-PAA-*b*-PEG was dissolved in water and gently agitated by a magnetic stirrer at room temperature till a clear solution was obtained. The solution was then transferred to a volumetric flask to obtain a stock solution with a concentration of 1 $g \cdot L^{-1}$. The pH was maintained at around 9 using dilute NaOH solution. A specific amount of calcium chloride (2.3 M, 0.1 mL) was added to PS-*b*-PAA-*b*-PEG micelle solution. The resulting solution was magnetically stirred to accelerate the interaction between the micelles and the metal ions. Disodium phosphate was added to the mixture to create CaP in the PAA layer of the polymeric micelles. The reaction mixture was stored under a quiescent condition for 12 hours in order to form the CaP/PS-*b*-PAA-*b*-PEG nanocomposites. The CaP/PS-*b*-PAA-*b*-PEG nanocomposite particles were collected by centrifugation at 5000 rpm. The composite particles were repeatedly washed with water and dried in an oven at 50 °C. To obtain the hollow CaP nanospheres, the polymer template was calcined at 500 ºC for 4 hours at ramping rate of 1 $^{o}C \cdot min^{-1}$.

Cell culture: BT-20 human breast cancer cells (ATCC® Number: HTB-19™) were used in this study. They were cultured in flasks with the MEM medium supplemented with 10 % fetal bovine serum, 2 % sodium bicarbonate, 1 % L-Glutamine, and 1 % penicillin at 37 °C under a humidified atmosphere containing 5 % CO_2.

Cell viability: Cell viability was investigated using MTT assay. First, BT-20 cancer cells were cultured in a 24-well culture plate at a density of 1.0×10^5 cells per well, and allowed to attach overnight. The cell-attached plate was then washed with PBS solution three times, and immersed in serum-free MEM medium (0.5 mL/well) containing different concentrations of hollow CaP nanoparticles. Fluorescein-adsorbed hollow CaP nanoparticles were used to examine the location of the hollow CaP nanoparticles in BT-20 cancer cells. Hollow CaP nanoparticles (0.02 g) were added into fluorescein isothiocyanate (FITC) aqueous solution (3 mL, 1.0×10^{-5} M). After stirring for 12 h, the product was collected by centrifuge at 5500 rpms for 30 mins. The FITC-adsorbed hollow CaP nanoparticles were then washed twice with water and dried in vacuum.

After incubation for 8 hours, the nanoparticle-immersed plate was washed several times with PBS solution to remove the nanoparticle residue. The MTT stock solution (5 mg/mL) was

then diluted 10 times with serum-free MEM medium and added to each well (0.5 mL/well). These cells were further incubated for 4 h to allow the yellow dye to transform into blue formazan crystals. The un-reacted dye was then removed by aspiration, and DMSO (400 μL) was added to each well to dissolve the blue formazan crystals. Finally, the dissolved DMSO solution was transferred to a 96-well culture plate (100 μL/well), and its optical density was measured with an Elisa Reader at a wavelength of 570 nm.

Figure S1

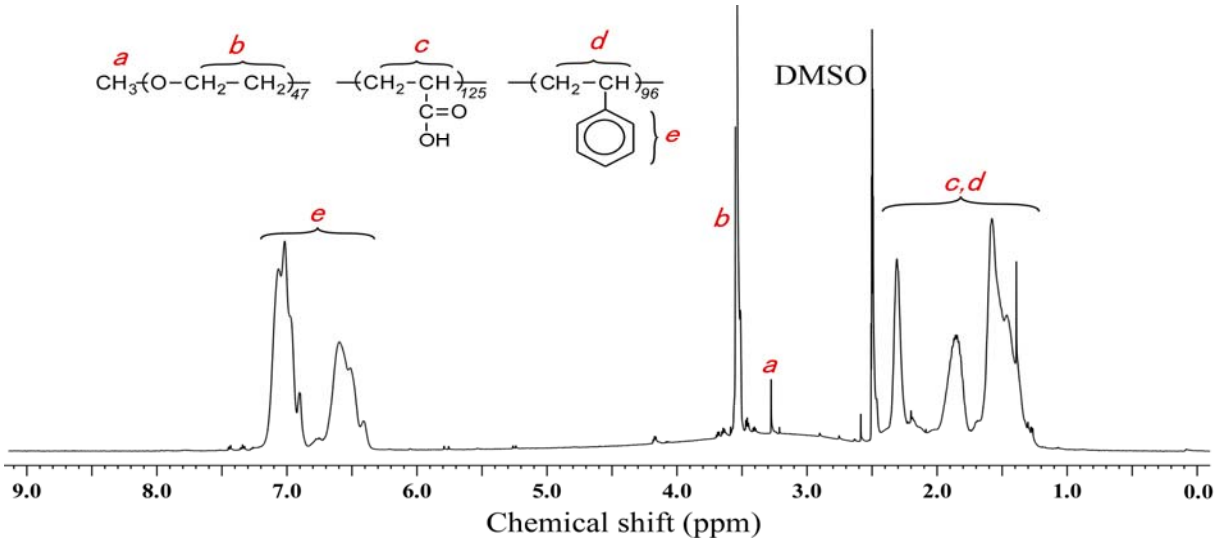

Figure S1 ^{1}H NMR spectrum in DMSO-d_6 at 100 ˚C for PEG_{47}-PAA_{125}-PSt_{96}

Figure S2

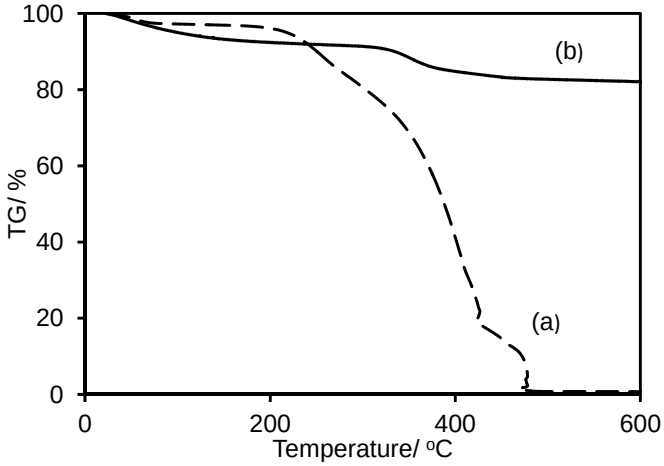

Figure S2 TG graphs of (a) polymer and (b) polymer -CaP nanocomposite particles.

Figure S3

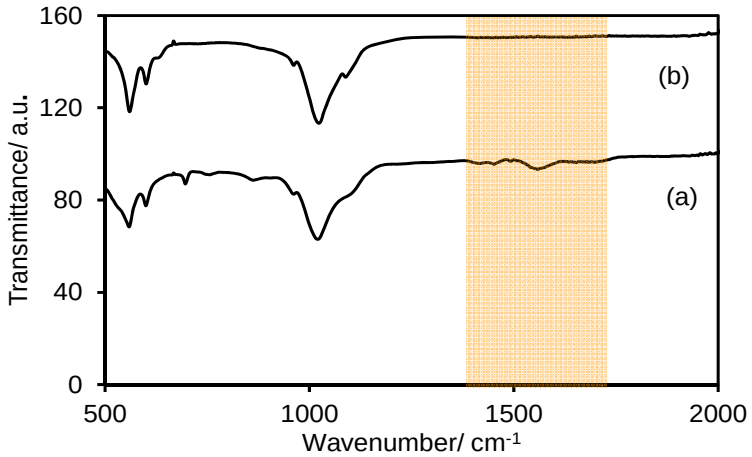

Figure S3 FT-IR spectra of hollow CaP nanospheres (a) before and (b) after removing the polymer template.

Figure S4

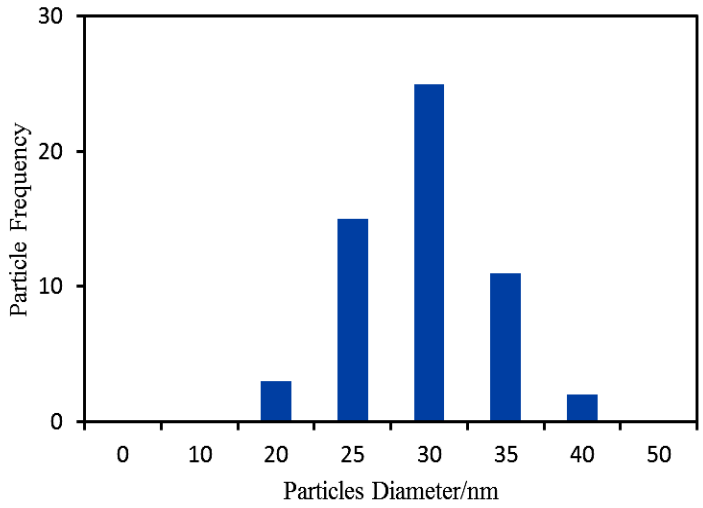

Figure S4 Particles size distribution of the obtained CaP hollow nanospheres.