Electronic Supplementary Information (ESI)

Figure S1 shows the effect of mass ratio between anionic polyelectrolyte and cationic polyelectrolyte on the particle size and zeta potential of ChS-HTCC system and ChS-CS system. Unlike ChS-HTCC system can formed NPs with positive or negative surface charge, ChS-CS system only can form positively charged NPs. The absolute value of zeta potential of ChS-CS NPs (pH 5.0) smaller than ChS-HTCC NPs in all mass ratio range of CS/HTCC between 1/4 and 4/1, these results indicated that ChS-HTCC system can formed more stable NPs than ChS-CS system in the same reaction condition. This is due to HTCC has the permanent cationic charges on the polysaccharide backbone; in contrast, the cationic charges of CS can be effected by the pH and the concentration of its counter ion.

**Figure S1.** The effect of mass ratio between anionic polyelectrolyte and cationic polyelectrolyte on the particle size and zeta potential of ChS-HTCC NPs (red and blue line) and ChS-CS NPs (green and magenta line). (▲) Method A; (●) Method B; (solid line) size; (dot line) zeta potential; Final concentration of HTCC or CS = 2 mg/ml;