Supporting Information

Cationic-anionic polyelectrolyte interaction as a tool to graft silver nanoparticles on hydroxyapatite crystals and prevent cytotoxicity.

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Figure S1. UV-vis spectrum of as-prepared AgNPs solution, which shows the surface plasmon resonance band of Ag nanoparticles at $\lambda_{max} = 405$ nm and should indicate a mean diameter of about 25 nm.



Figure S2. Powder X-ray diffraction patterns and IR spectra of HA and HAPAA. Samples obtained in the presence of polyacrylic acid are constituted of hydroxyapatite as unique crystalline phase, but show a reduced level of crystallinity evidenced both by the broadening of XRD reflections and by the lower intensity of OH⁻ FTIR bands. IR spectrum of HAPAA also shows the presence of PAA bands in the range 1720-1410 cm⁻¹.



Figure S3. Thermogravimetric plots of PAA and PEI. Both polyelectrolytes undergo complete combustion within 800°C.



Figure S4. Thermogravimetric plots of HA, HAPAA, HA-AgNPs and HAPAA-AgNPs. HA plot does not show any significant weight loss up to 900°C. Therefore, the weight losses of the composite materials can be attributed to the presence of polyelectrolytes. No difference was appreciable between the plots of HAPAA-AgNPs, at variable silver content (the same holds true for HA-AgNPs).



Figure S5. TEM images of HA and HAPAA crystals. HAPAA crystals exhibit reduced mean dimensions and a greater aspect ratio with respect to HA crystals.



Figure S6. Microscopic images of MG63 osteoblast cultures after 48 h of incubation. Neutral Red staining. Magnification: 10x. Each image reports the relative qualitative grade of cytotoxicity (according to Table S1).



Figure S7. Bacterial growth in incubation media of HAPAA10 at 6 h (a,b) and 24 h (c,d) of *S. aureus* and *E. coli*.



Figure S8. Release of silver from disk-shaped samples of HAPAA10 as a function of the storage time in Luria-Bertani medium. The standard deviation is reported just when the bars exceed the size of the symbols.

grade	reaction	condition of cultures
0	none	No cell lysis, no reduction of cell growth, discrete intercytoplasmatic granules.
1	slight	Not more than 20% of the cells are round, loosely attached and without intercytoplasmatic granules, or show changes in morphology; occasional lysed cells, slight growth inhibition.
2	mild	Not more than 50% of the cells are round, devoid of intercytoplasmatic granules, cell lysis and not more than 50% growth inhibition.
3	moderate	Not more than 70% of the cells are round and lysed, more than 50% growth inhibition.
4	severe	Nearly complete or complete destruction of the cell layer.

 Table S1. Qualitative morphological grading of cytotoxicity.