

Supporting Information

Dual functional polylactide-hydroxyapatite nanocomposites for bone regeneration with nano-silver being loaded via reductive polydopamine

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Preparation of m-HA/Ag

To optimize the preparation of m-HA/Ag, different silver ion concentration and reaction time were applied to achieve efficient loading of AgNPs onto m-HA. Briefly, m-HA (1 g) was dispersed in 100 mL deionized water and different amounts of AgNO₃ were added (**Table S1**), and the reaction time was fixed at 4 h. Or m-HA (1 g) was dispersed in 100 mL deionized water and AgNO₃ (0.05 g), and the reaction time was set as 1 h, 4 h and 24 h (**Table S1**), respectively. At the end of the reaction, the suspensions were centrifuged to collect m-HA/Ag. After being washed with deionized water and freeze-dried, the obtained m-HA/Ag powders were submitted to TGA measurement in nitrogen atmosphere to determine the loaded amount of AgNPs.

As shown in **Fig. S1**, the loading amounts of AgNPs onto m-HA increased gradually as the reaction time being prolonged, or as the silver ion concentration being increased. The effect of reaction time was found more efficient in raising the AgNPs loading than that of silver ion concentration. Among these preparations, the highest loading amount of AgNPs was achieved in sample of m-HA/Ag-3, ~2.7 wt.%. In the following studies on PLLA/HA/Ag nanocomposites, however, m-HA/Ag-2 was

used. The concern is that high content of AgNPs being incorporated into PLLA/HA/Ag nanocomposites might cause significant cytotoxicity to BMSCs.

Table S1 Different designs on preparation of m-HA/Ag.

Samples	AgNO ₃ concentration (mg/mL)	Reaction time (h)
m-HA/Ag-1	0.5	1
m-HA/Ag-2	0.5	4
m-HA/Ag-3	0.5	24
m-HA/Ag-4	1	4
m-HA/Ag-5	2	4

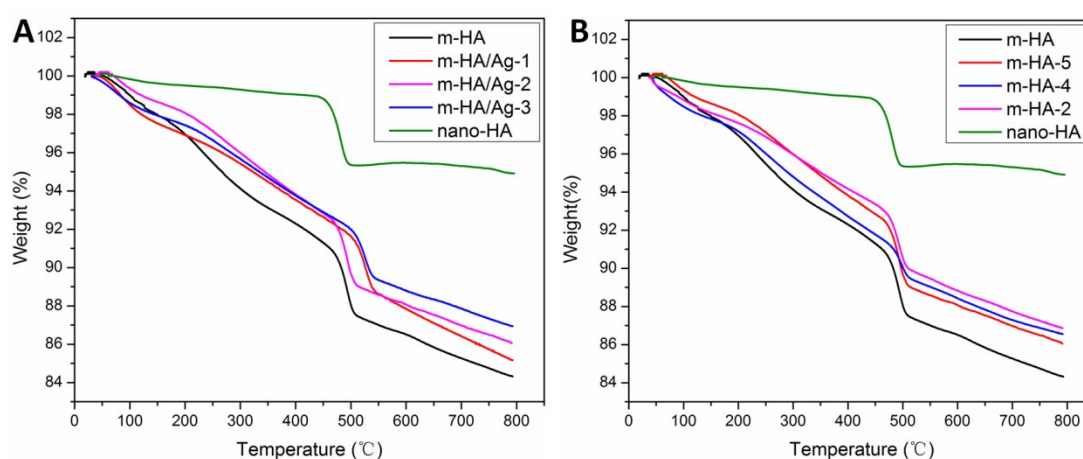


Fig. S1 TGA curves of various m-HA/Ag_s prepared from different designs in comparison with original nano-HA and PDA-modified m-HA: (A) different reaction times; (B) different AgNO₃ concentrations.

Dispersibility of m-HA/Ag

After AgNPs being loaded onto m-HA, the dispersibility of m-HA/Ag in chloroform was examined by TEM (see **Fig. 3** in the main text) and dynamic light scattering (DLS) analysis (**Fig. S2**). Briefly, the obtained m-HA/Ag was dispersed in chloroform (0.1 wt. %) for 0.5 h, 24 h and 48 h, respectively, and then the suspensions were submitted to size distribution analysis by using a BI-90Plus (Brookhaven, USA) with a solid laser (35 mW). As shown in **Fig. S2**, two average particle sizes were detected shortly after the suspension was prepared (0.5 h). However, only one average particle

size around 700 nm was detected after the suspension had been magnetically stirred for another 48 h, indicating the good dispersibility of m-HA/Ag with narrow particle size distribution. These data were consistent with those reported DLS results in our previous work.¹ The explanation was proposed to the gradual swelling of the PDA coating layer on HA surface, and the PDA chains achieved a fully stretched state by being soaked in chloroform for 2 days. The final particle size was the HA nanoparticle with its swollen PDA surface layer, accordingly, aggregation of nano-HAs was prevented and uniform particle size was detected. Besides, the loading of AgNPs did not cause adverse effect on the dispersibility.

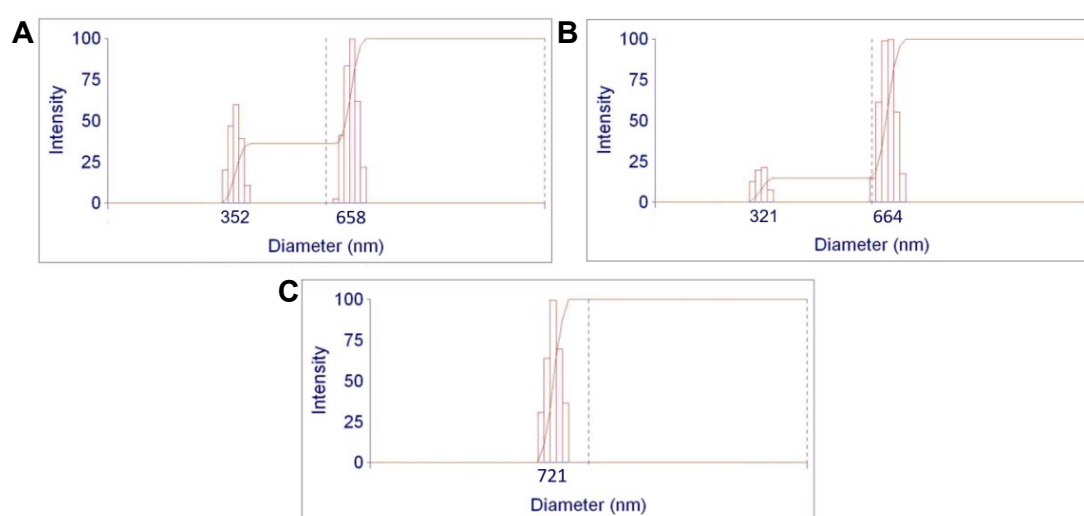


Fig. S2 Analysis on particle size and particle size distribution of m-HA/Ag by DLS, and the data in (A-C) indicate the particle size and particle size distribution of m-HA/Ag after they were dispersed in chloroform for 0.5 h (A), 24 h (B) and 48 h (C).

Tensile properties of PLLA/HA/Ag nanocomposite film

PLLA/m-HA and PLLA/HA/Ag nanocomposite films were prepared and submitted to tensile measurements. The purpose was to identify that the incorporation of AgNPs will not weaken the mechanical properties of PLLA/m-HA. To do the comparison, m-HA or m-HA/Ag-2 was mixed into PLLA/CHCl₃ solution at the weight ratio of 30 wt.% referring to the total weight of PLLA and HA. Nanocomposite films were obtained by casting the suspensions onto glass plate and thorough solvent evaporation. According to standard ISO 527-3:1995, the films were cut into dumbbell-shaped specimens with effective dimensions of 20 mm in length and 4 mm

in width. The thickness of each specimen was measured by a digital thickness meter. Then the tensile properties of both PLLA/m-HA and PLLA/HA/Ag specimens were determined with an Instron 1211 machine by applying a 50 N load cell at a stretching speed of 10 mm/min.

As shown in **Fig. S3**, with the loading of AgNPs, both the tensile strength and elongation of PLLA/HA/Ag nanocomposite film demonstrated slight decreases in comparison with those of PLLA/m-HA nanocomposite film. Promisingly, however, no significant difference was identified between the two nanocomposite films. The results indicated that the introduction of a small amount of AgNPs into the PLLA/m-HA nanocomposite would not cause much adverse effect on its mechanical properties.

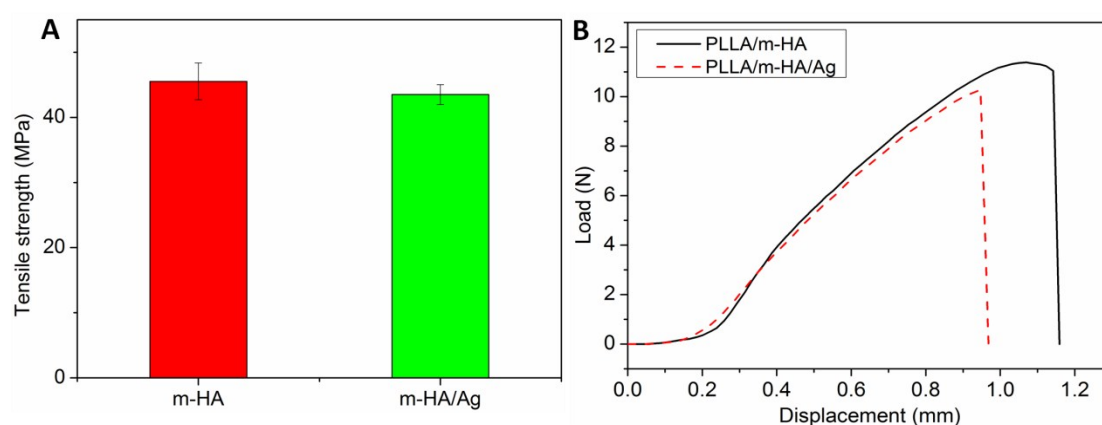


Fig. S3 Tensile strength (A) and tensile stress-strain curves (B) of PLLA/m-HA and PLLA/HA/Ag nanocomposite films containing 30 wt.% of m-HA and m-HA/Ag-2, respectively.

Reference

1 H. Sun, M. Ai, S. Zhu, X. Jia, Q. Cai and X. Yang, *RSC Adv.*, 2015, **5**, 95631-95642.