Supporting Information:

S1. Role and evidence of GA crosslinking in layer-by-layer nanoassembly:

S1.1. Evidence of aldehyde groups on the surfaces of $(PLL/PLGA)_{3.5}$-GA-shelled $CaCO_3$ particles

Tollens mirror reactions were carried out to confirm the existence of aldehyde groups[1] on the surfaces of $(PLL/PLGA)_{3.5}$-shelled $CaCO_3$ particles after treating with GA, i.e. $(PLL/PLGA)_{3.5}$-GA-shelled $CaCO_3$ particles. One ml of silver nitrate solution (2 mg/ml) was added to three vials of suspensions with $(PLL/PLGA)_{3.5}$ -, $(PLL/PLGA)_{3.5}$-GA- and $(PLL/PLGA)_{3.5}$-GA-PLL-shelled particles followed by several drops of sodium hydroxide solution. Brown precipitates were observed in the three vials. Next, 1 M ammonia was added dropwise, with stirring, to the three vials until the solutions became clear. The three vials were then immersed in a water bath (50^oC) for 10 min. The Tollens reaction was observed only in the suspension of $(PLL/PLGA)_{3.5}$-GA-shelled particles; silver precipitates were formed in the suspension of $(PLL/PLGA)_{3.5}$-GA-shelled particles but not in the other two particle suspensions (**Fig. S1**). This confirmed that there were aldehyde groups on $(PLL/PLGA)_{3.5}$-GA-shelled particles due to the use of excessive GA. No obvious mirror was observed in the suspension of $(PLL/PLGA)_{3.5}$-GA-shelled particles, which was probably due to the relatively low concentration of aldehyde groups on $(PLL/PLGA)_{3.5}$-GA-shelled particles.

Fig. S1. Tollens mirror reaction of (left) $(PLL/PLGA)_{3.5}$-, (middle) $(PLL/PLGA)_{3.5}$-GA-, and (right) $(PLL/PLGA)_{3.5}$-GA-PLL-shelled particles. Excessive PLL was used to react with the aldehyde groups of GA in the last step in forming $(PLL/PLGA)_{3.5}$-GA-PLL-shelled particles. As a result, no aldehyde groups remain in $(PLL/PLGA)_{3.5}$-GA-PLL-shelled particles.

S1.2. Effect of GA crosslinking on assembly of shelled $CaCO_3$ particles on polypeptide multilayer films

Fig. S2 shows that GA led to the substantial assembly (1.8×10^6 /cm^2) of shelled $CaCO_3$ particles

on $(PLL/PLGA)_{3.5}$; by contrast, very few particles were deposited on polypeptide multilayer films without GA.

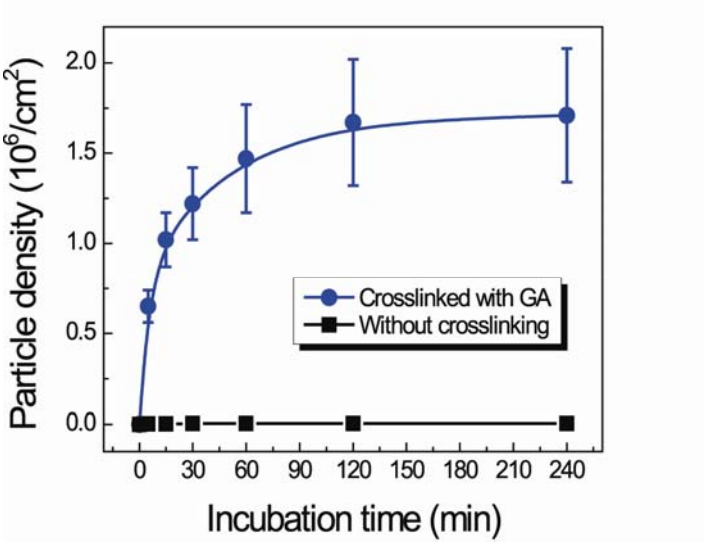

Fig. S2. Density of $(PLL/PLGA)_{3.5}$ shelled $CaCO_3$ particles, with and without GA crosslinking, assembled in polypeptide multilayer films *vs.* incubation time in a $CaCO_3$ particle suspension (2×10^8 particles/ml).

S1.3. FTIR spectra of $(PLL/PLGA)_{3.5}$, $(PLL/PLGA)_{3.5}$-GA and $(PLL/PLGA)_{3.5}$-GA-PLL shelled Capsule^{PLL}

The peak at 1660 cm^{-1} of $(PLL/PLGA)_{3.5}$ and $(PLL/PLGA)_{3.5}$-GA-PLL shelled capsules is attributed to the C=O stretch in PLL and PLGA. Blue shift (1640 cm^{-1}) in the $(PLL/PLGA)_{3.5}$-GA sample might be attributed to the aldehyde groups in the $(PLL/PLGA)_{3.5}$-GA capsule; no aldehyde groups are expected in $(PLL/PLGA)_{3.5}$ and $(PLL/PLGA)_{3.5}$-GA-PLL shelled capsules (**Fig. S3**).

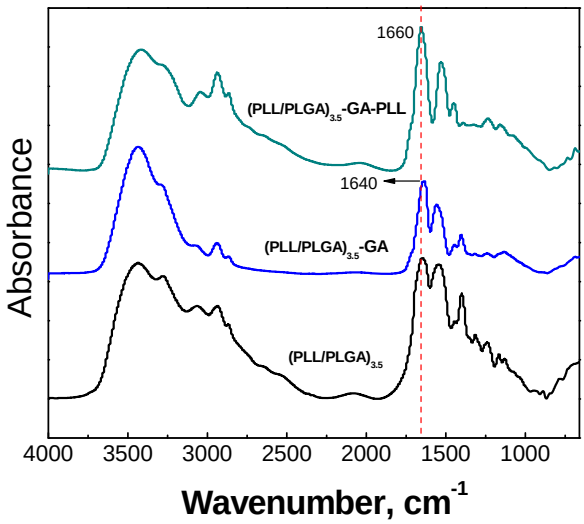

Fig. S3. FTIR spectra of $(PLL/PLGA)_{3.5}$, $(PLL/PLGA)_{3.5}$-GA and $(PLL/PLGA)_{3.5}$-GA-PLL shelled $Capsule^{PLL}$. Excessive PLL was used to react with the aldehyde groups of GA in forming $(PLL/PLGA)_{3.5}$-GA-PLL-shelled $Capsule^{PLL}$. As a result, no aldehyde groups are expected in $(PLL/PLGA)_{3.5}$-GA-PLL-shelled $Capsule^{PLL}$.

S2. Loading of FITC-BSA into $(PLL/PLGA)_{3.5}/Capsule^{PLL}/(PLL/PLGA)_{10.5}$ films

Fig. 4S showed that FITC-BSA was loaded into the capsules, since within a short time period (e.g. 20 sec), the fluorescence intensity on the capsule edges was higher than that in the capsule center, and after 15 min, the fluorescence intensity in the capsule center was much higher than those on the capsule edges.

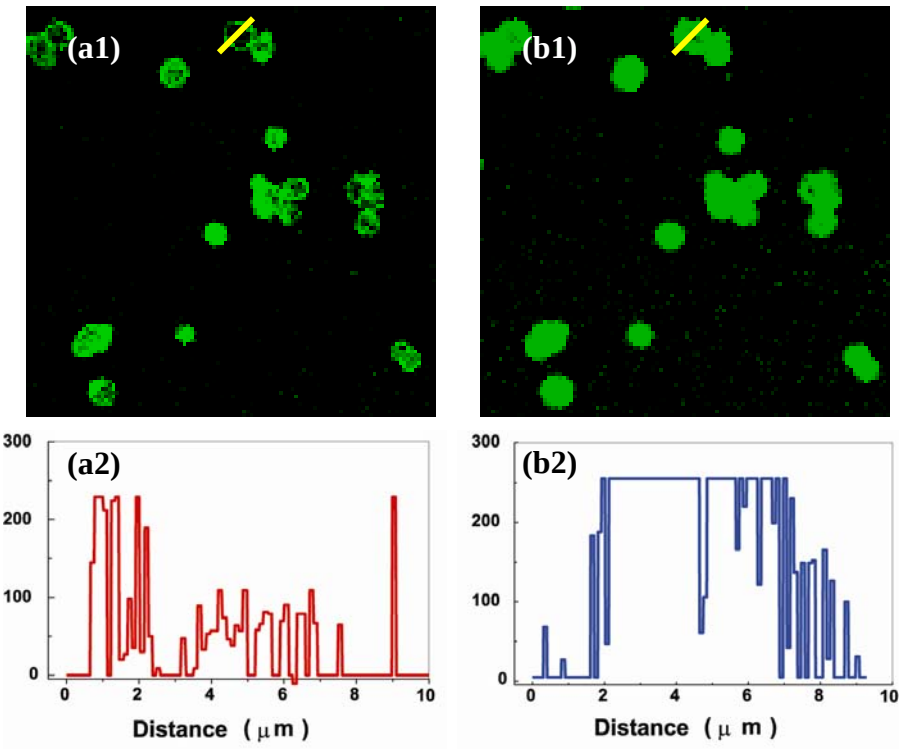

Fig. S4. Fluorescence images and intensity profiles of a randomly selected single capsule (marked by the yellow line) within polypeptide multilayer films of $(PLL/PLGA)_{3.5}/Capsule^{PLL}/(PLL/PLGA)_{10.5}$ that was loaded with FITC-BSA for (a1, a2) 20 sec and (b1, b2) 15 min, respectively. Y-axis represents fluorescent intensity.

Reference:

(1). Saito, Y.; Wang, J. J.; Smith, D. A.; Batchelder, D. N. *Langmuir* **2002**, *18*, 2959-2961.