Supporting Information

Hollow protein microparticles through cross-linking by Au^{3+} initiated redox reaction

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S1 Additional CLSM image of $CaCO_3$ encapsulating HDL

A 3D construct of a series of Z-stack images of the FITC-labelled HDL encapsulated in $CaCO_3$ templates allowed to visualize the localization of HDL throughout the templates. Figure S1 shows that the fluorescent signal of the FITC-labelled HDL is present throughout the whole template, but not homogeneously distributed.

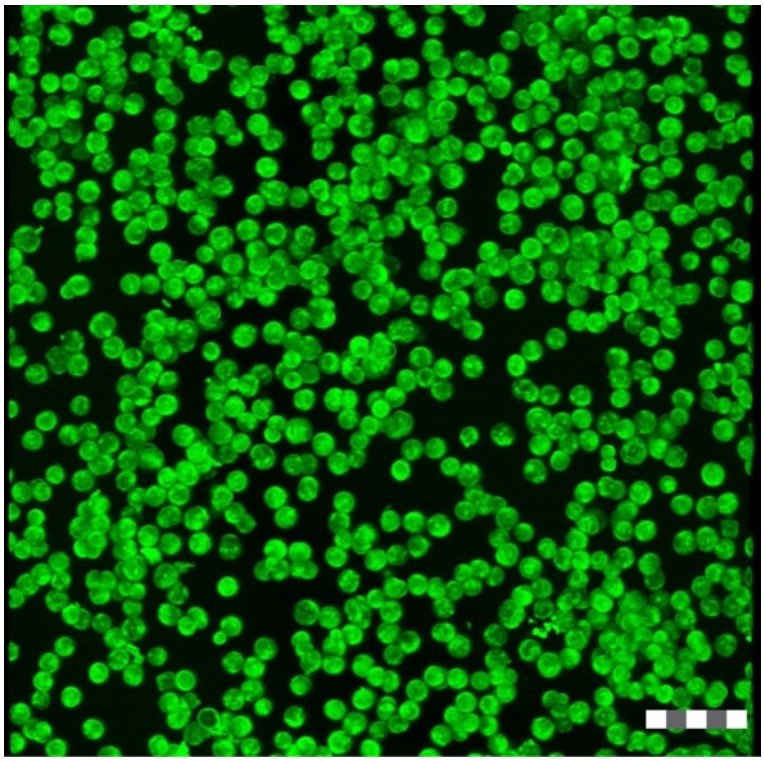

Figure S1. CLSM Z-stack (3D reconstruction) of FITC-labelled HDL encapsulated in $CaCO_3$ templates (scale bar is 25 μm).

S2 Zero surface charge point of HDL

To determine the point of zero surface charge of HDL, zeta-potential measurements were done on HDL solutions at pH 2-12. The zeta-potential as a function of pH showed that the zero surface charge point of HDL is at pH 5.6.

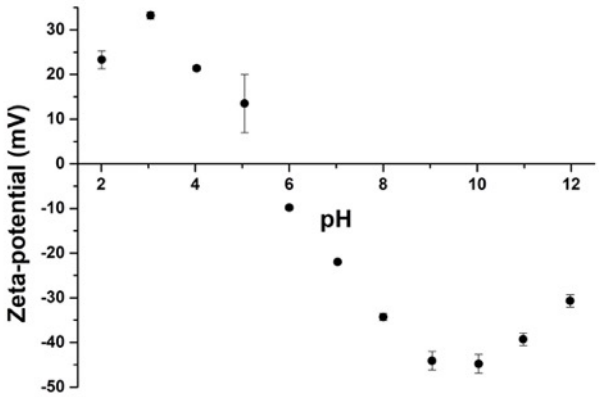

Figure S2. The effect of pH on zeta-potential of HDL, the point of zero surface charge was found at pH 5.6.

S3 Additional CLSM and TEM images of HDL-MPs

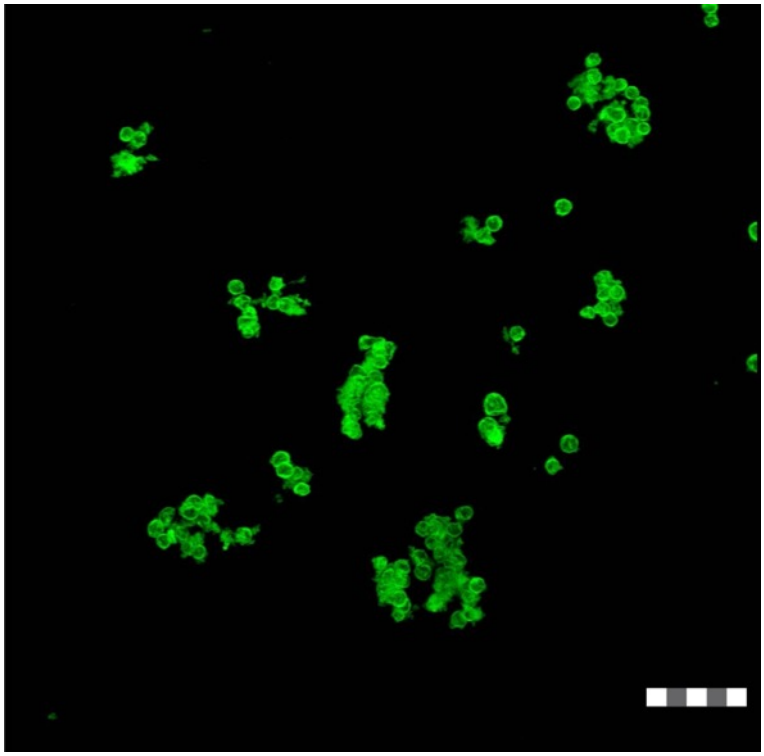

Figure S3. CLSM Z-stack (3D reconstruction) of FITC-labelled HDL-MPs (scale bar is 25 μm).

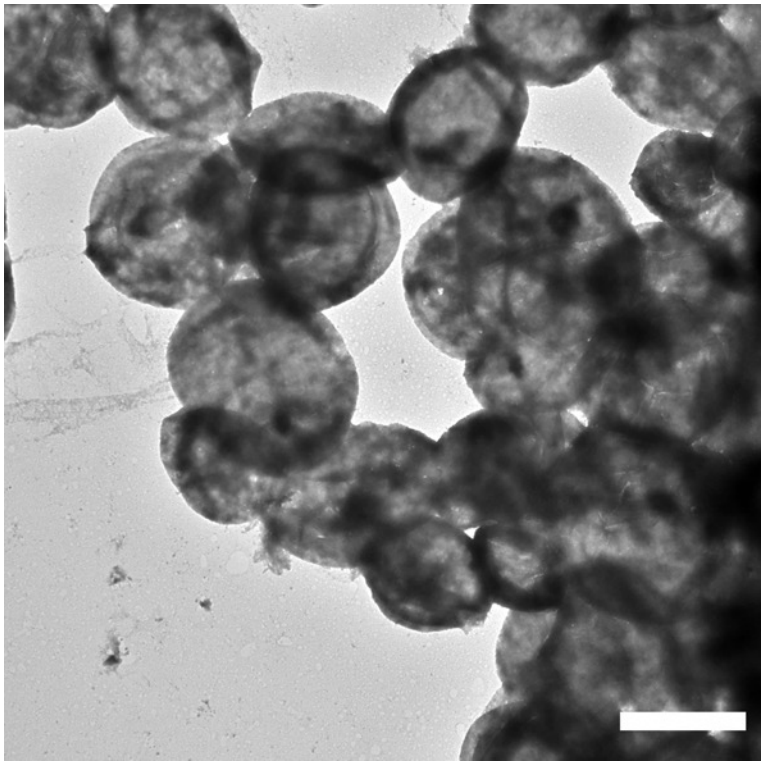

Figure S4. Overview TEM image of HDL-MPs, scale bar is 5 μm.

S4 Following the synthesis of AuNPs in time

Au^{3+} ions were added to $CaCO_3$ encapsulating HDL. Initially, the $CaCO_3$ encapsulating HDL were yellow colored (Figure S5 A, t = 0 and 0.5 h). The $CaCO_3$ encapsulating HDL gradually changed from yellow to pink, then to red as growth proceeded (t = 2-5 h). When the $CaCO_3$ flocculated, the solutions were transparent and the precipitates were colored (Figure S5 B). The color evolution of the $CaCO_3$ encapsulating HDL originates from the characteristic LSPR absorption of AuNPs, indicating the formation and growth of AuNPs inside the $CaCO_3$ templates. When the templates were removed, the Au-HDL-MPs were stable in solution and retained their red color (Figure S5 C) The LSPR absorption of the AuNPs was confirmed by UV-Vis absorbance spectra, which demonstrated the appearance and increase of absorption peaks in time in the region of λ = 500-600 nm (Figure S5 D).

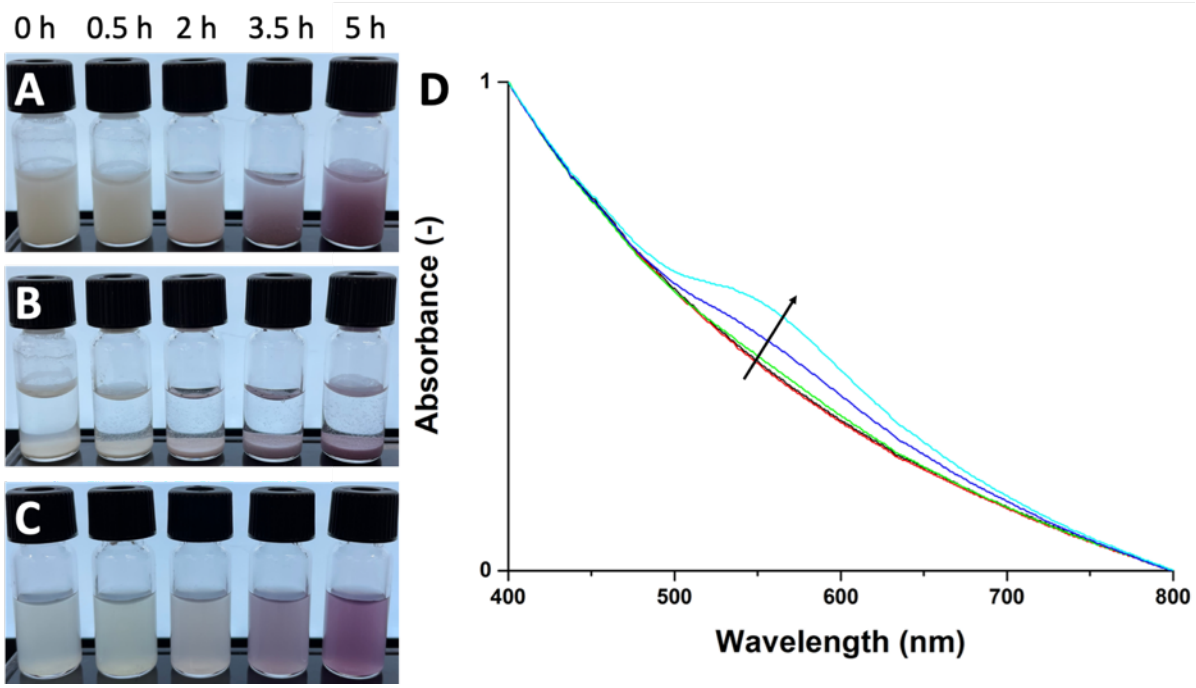

Figure S5. Pictures of (A) suspended and (B) flocculated Au-HDL-MPs in $CaCO_3$ templates and (C) Au-HDL-MPs released from the templates at time points of 0-5 h. (D) Normalized UV-Vis absorbance spectra of Au-HDL-MPs showing a clear red shift of the LSPR peaks in time, as indicated by the arrow. The spectra were normalized at λ = 400 nm. Samples were taken at t = 0, 0.5, 2, 3.5 and 5 h.

S5 Additional CLSM and TEM images of Au-HDL-MPs

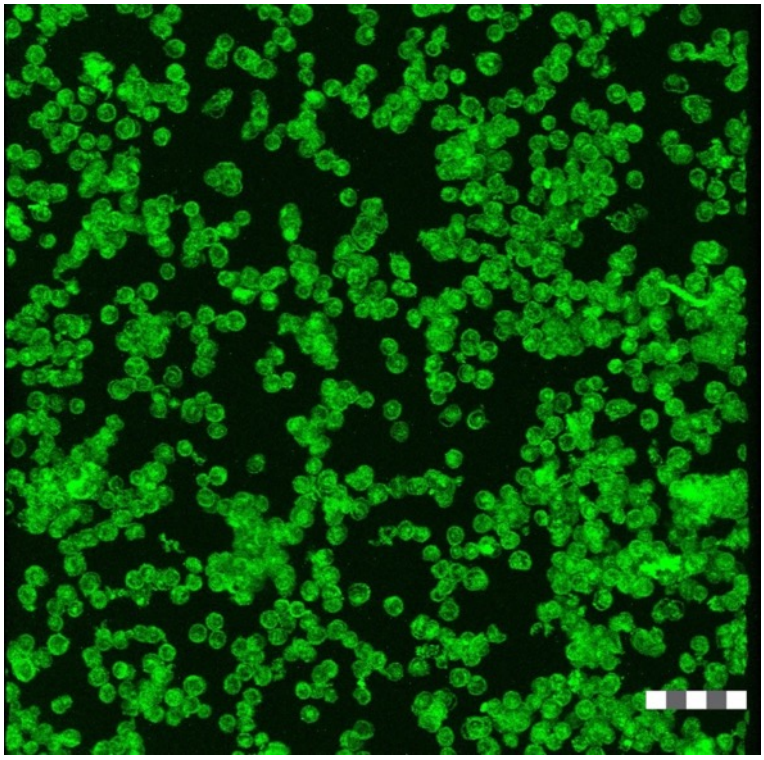

Figure S6. CLSM Z-stack (3D reconstruction) of FITC-labelled Au-HDL-MPs (scale bar is 25 μm).

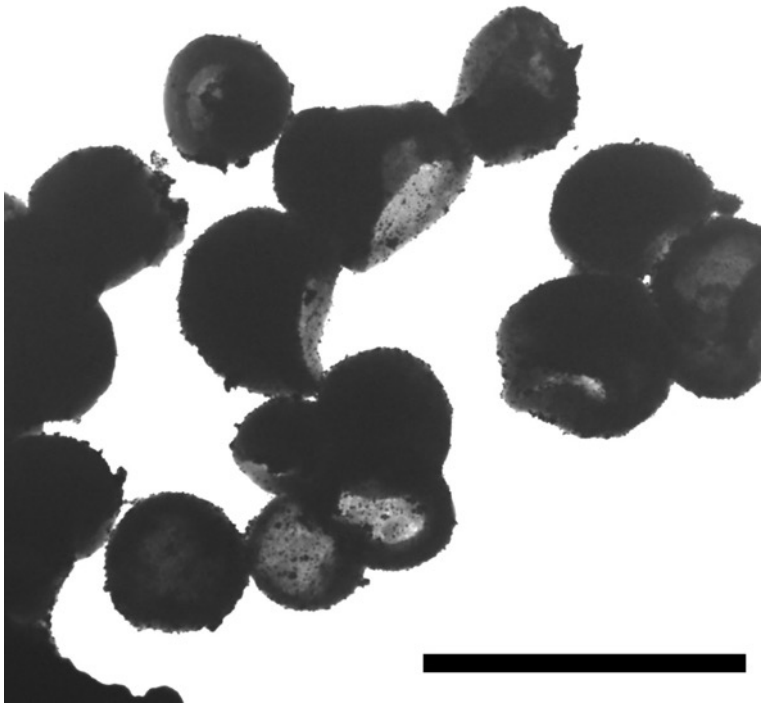

Figure S7. Overview TEM image of Au-HDL-MPs, scale bar is 5 μm.