

Electronic Supplementary Information for

A Facile Ligand-Free Route to Calcium Carbonate Superstructures

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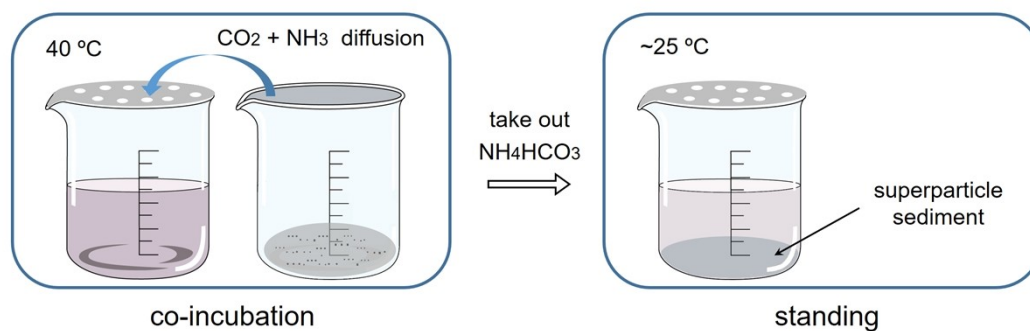


Figure S1. Scheme of the synthesis process of CaCO₃ superparticles.

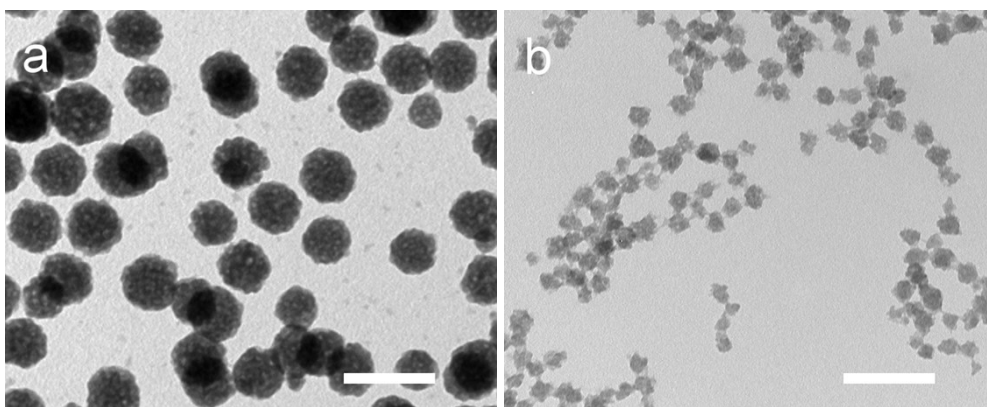


Figure S2. TEM images of primary CaCO_3 nanoparticles obtained when (a) 0 mL or (b) 0.25 mL of water was added into the 50 mL ethanol reaction solution followed by a standard 24 of incubating reaction. Scale bar: 200 nm.

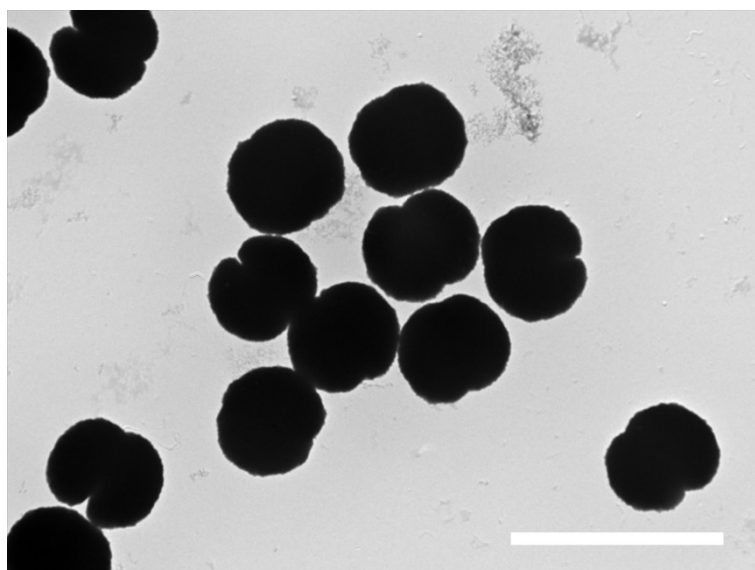


Fig. S3 TEM image of CaCO_3 superparticles obtained after 12 days of post-incubation standing, suggesting the formation of quasi-spherical particles. Scale bar: 5 μm .

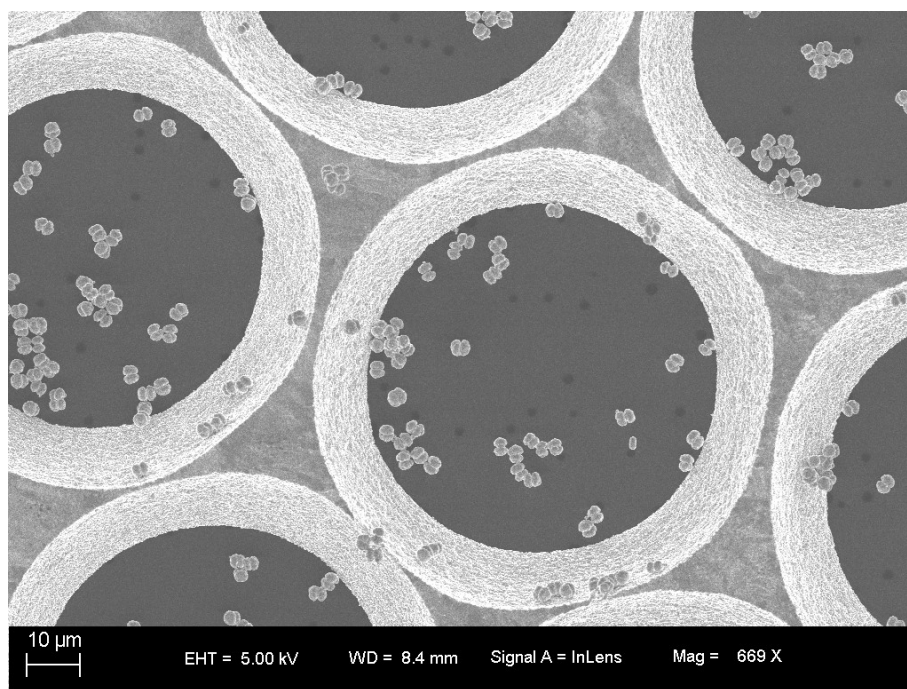


Fig. S4 Large-field SEM image of double-semisphere-shaped CaCO₃ superparticles on a copper grid.

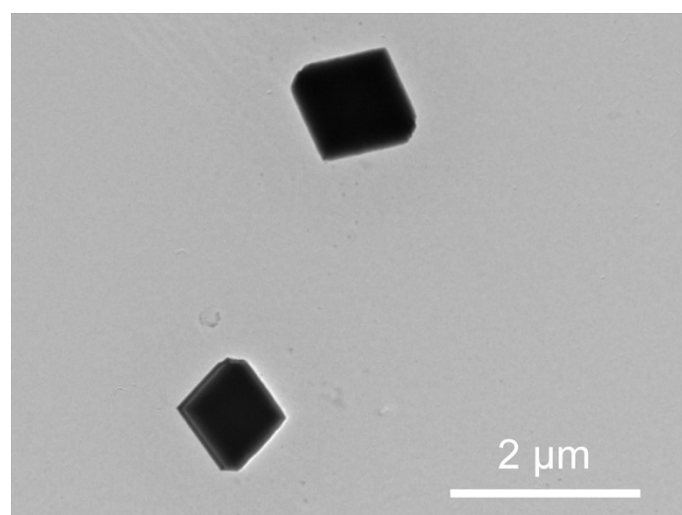


Fig. S5 Representative TEM image of CaCO₃ particles obtained at H₂O/EtOH of 3% in volume.

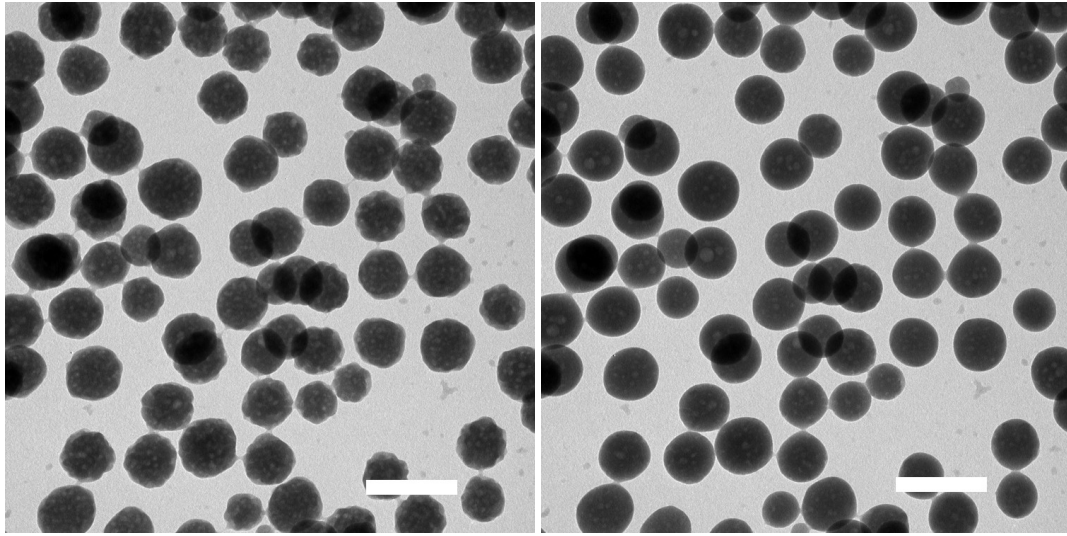


Fig. S6 TEM images showing the morphological and structural transition of CaCO_3 nanoparticles under the irradiation of electron beam during TEM imaging process: (a) a field quickly imaged and (b) the same field imaged after irradiated for seconds. Scale bar: 200 nm.

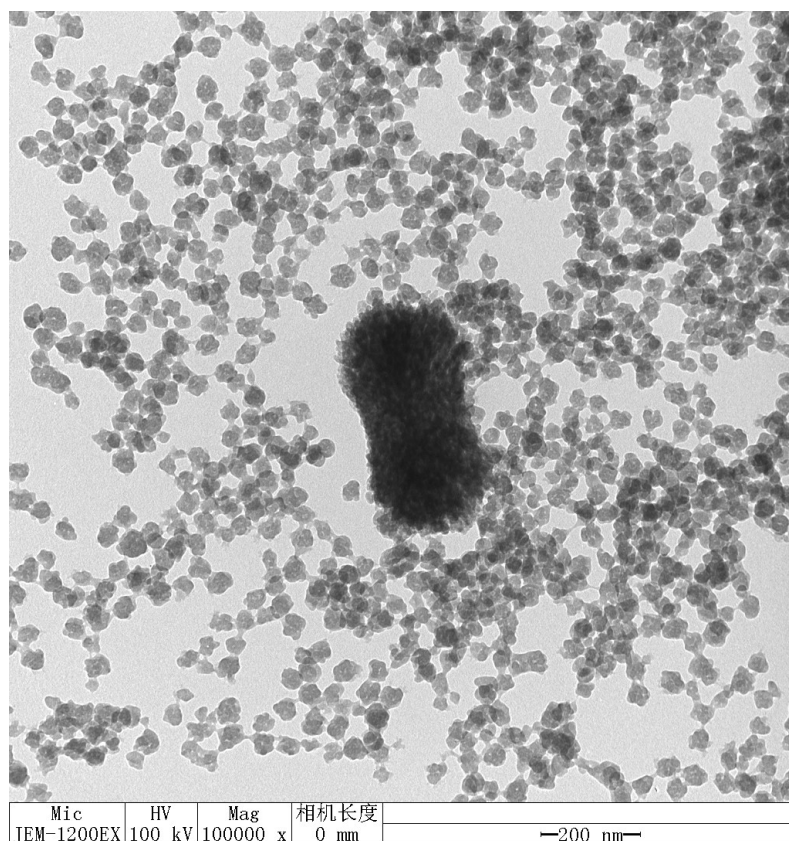


Fig. S7 TEM image of a rod-like particle formed at the initial stage of superparticle formation, clearly showing that i) the constituent grains were much smaller than primary NPs, and ii) the grains of the rod-like particle took a centrifugal alignment.

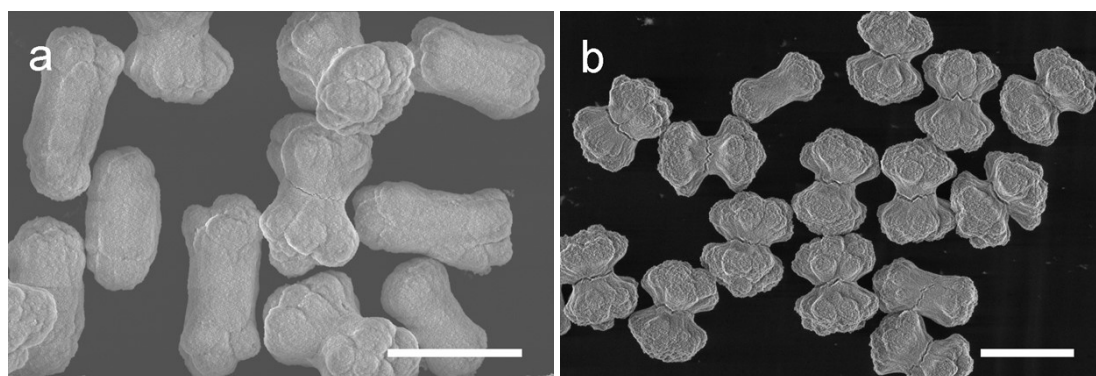


Fig. S8 SEM images of (a) rod-like particles and (b) dumbbell-shaped particles, showing that many of the initial rod-like particles do not have cracks, while nearly every dumbbell-shaped particle has a crack. Scale bar: 2 μm .

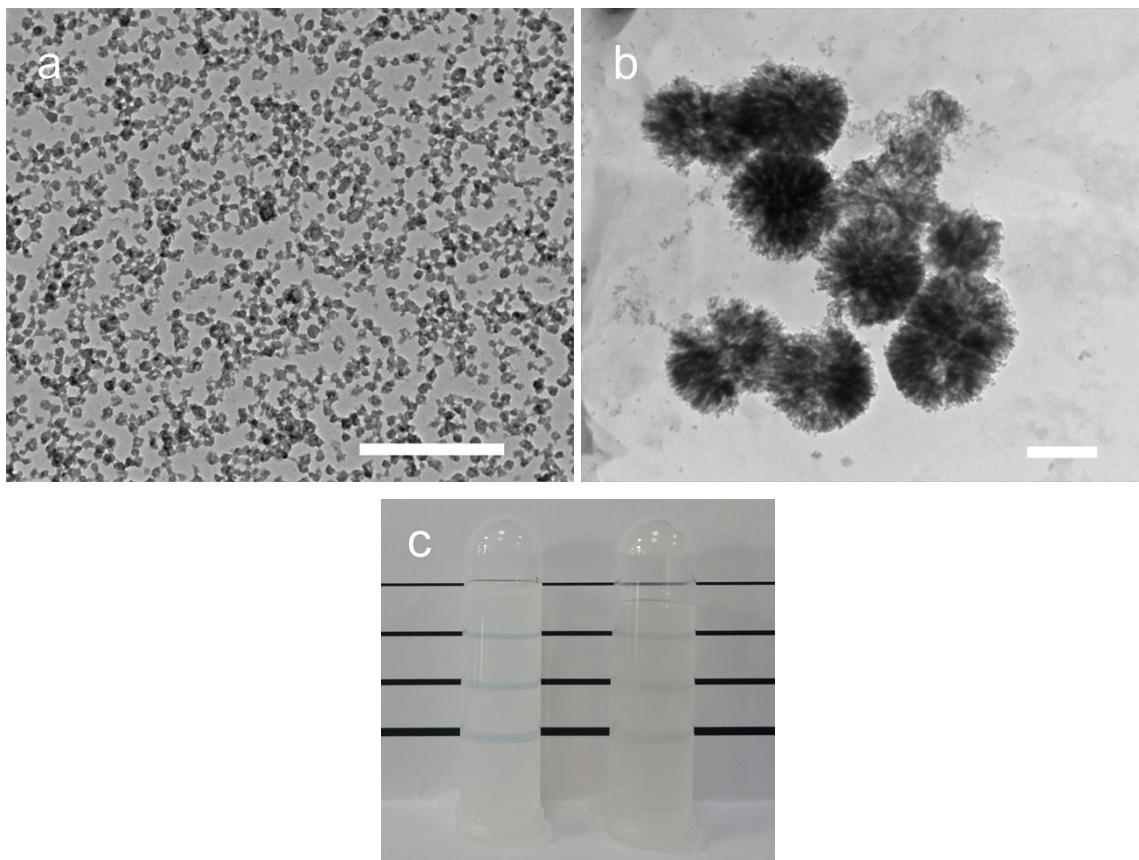


Fig. S9 TEM imaging results demonstrating the morphology transition of CaCO_3 primary NPs when dispersed in (a) ethanol and then in (b) H_2O . Scale bar: 500 nm. (c) Photographs of primary NPs dispersed in (left) ethanol and (right) H_2O , showing that NPs were well-dispersed in ethanol but not in H_2O .

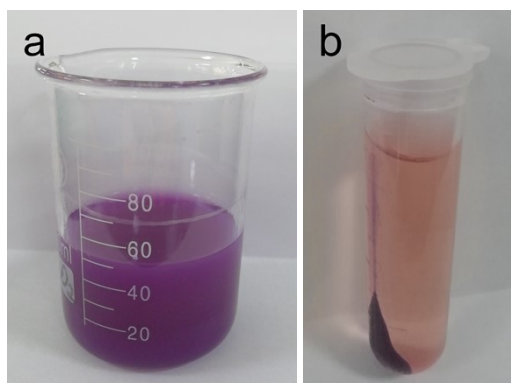


Fig. S10 Photographs of (a) reaction beaker containing Dox@CaCO₃ primary NP dispersion obtained after 24 of incubation reaction (Dox/CaCl₂·H₂O: 3% in weight; H₂O/EtOH: 0.5% in volume), and (b) an Eppendorf tube containing the same dispersion after centrifuged at 8000 rpm for 5 min.

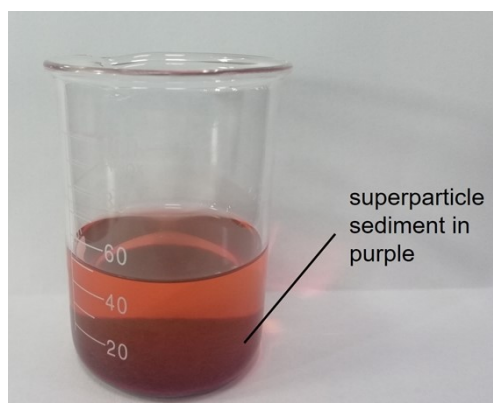


Fig. S11 Photographs of a reaction beaker containing Dox@CaCO₃ superparticles. Particle sedimentation is a typical indication of the formation of superparticles, while the purple color of sediment shows the efficient Dox incorporation into superaprticles.

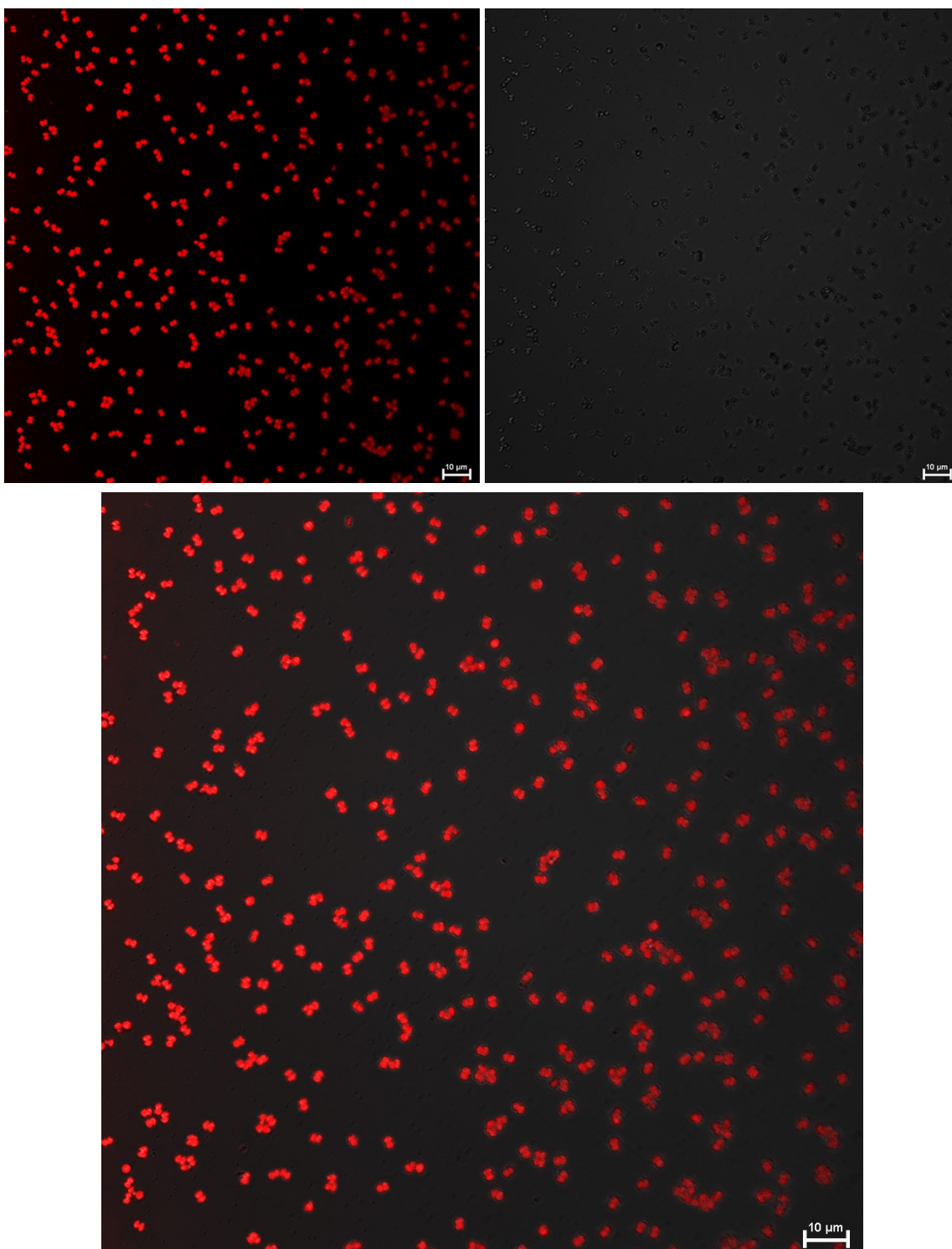


Fig. S12 Confocal laser scanning microscopy images of Dox-embedded CaCO₃ superparticles: upper, fluorescence (left) and bright field (right) images; lower, the merged image.

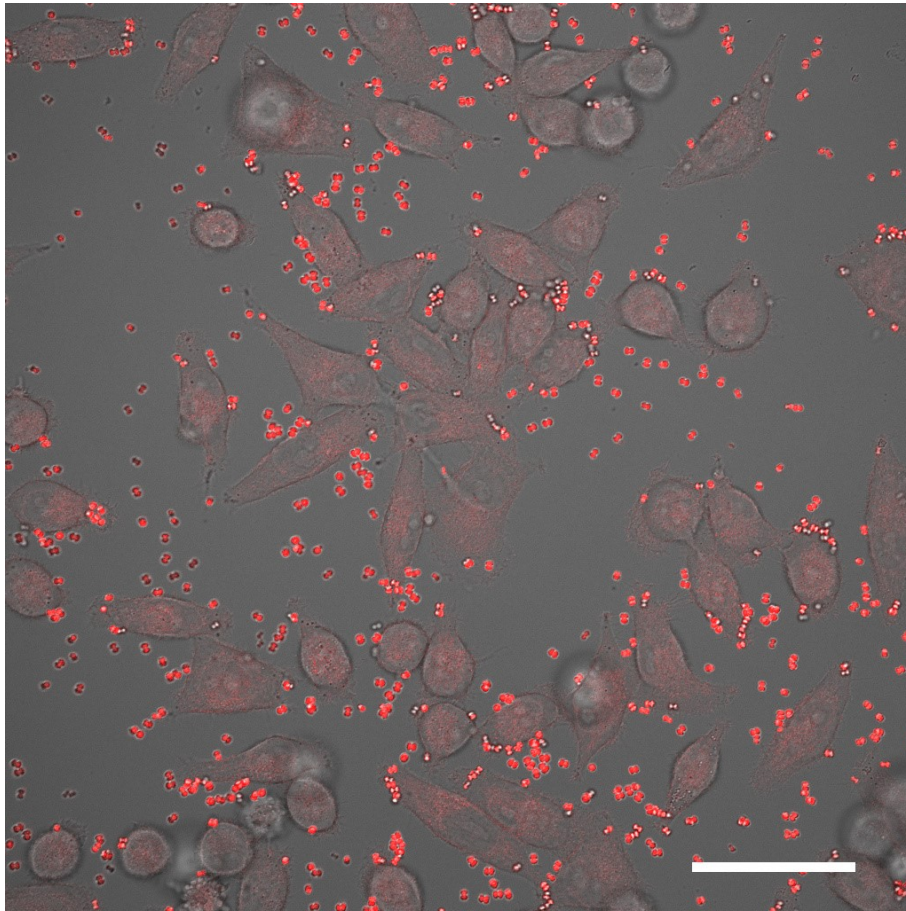


Fig. S13 Enlarged CLSM image of MCF-7 cells after co-incubated with Dox@CaCO₃ superparticles for 0.5 h. Scale bar: 50 μ m.