Fabrication of Au@ CaCO₃ Nanoparticles by in-situ Mineralization in Hydrogel Microspheres

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Supporting Information:

Experimental Section:

Materials. N-isopropyl acrylamide (NIPAM), N,N'-methylenebisacrylamide (MBA), methacrylic acid (MAA), potassium persulfate (K₂S₂O₈), calcium chloride (CaCl₂), ammonium carbonate ((NH₄)₂CO₃), chloroauric acid (HAuCl₄), and sodium citrate were purchased from Sigma-Aldrich. NIPAM was purified by re-crystallization from a toluene/hexane mixture (1:3); MAA was purified by distillation under vacuum. Other commercial materials were used without further purification.

Synthesis of Au Nanoparticles. 12 nm Au NPs were prepared by citrate reduction of HAuCl₄ in the presence of citrate acid ¹. Typically, 10 mL 1% (w/v) sodium citrate solution was added into a boiling solution of 290 mL 0.015% (w/v) HAuCl₄. Within 3 min the solution turned out wine-red, indicating the formation of Au NPs. After further boiling for 10 min, the heat source was removed and the dispersion was cooled down to room temperature. The Au NPs obtained were about 16 nm in size, determined by means of TEM and DLS. They exhibit a distinct surface plasmon absorption band, centred at 520nm.

Synthesis of PNIPMAA Spheres. PNIPMAA spheres were prepared by a surfactant-free emulsion polymerization described elsewhere ². Typically, 250 mg of NIPAM, 10 mg of MAA, 20 mg of K₂S₂O₈, and 25 mg of MBA were dissolved in 25 mL of de-ionized water in a 50 mL vial. The polymerization was carried out for 4 h at 70°C under a nitrogen atmosphere. The PNIPMAA spheres were purified by conducting successive centrifugation at 8000g for 10 min (Beckman preparative ultracentrifuge), decantation, and re-dispersion in deionized

water for 4 times. PNIPMAA spheres are about 1010 nm in diameter at pH 7 and room temperature, as determined by DLS.

Loading Au NPs within PNIPMAA Spheres.² PNIPMMA hydrogel spheres were incubated within suspensions of 16 nm citrated-stabilized Au NPs. The volume ratio of the gel to the NP dispersions was set as 1:3. After incubation at pH 7 and room temperature for 5 min, followed by repeating the cycle of centrifugation at 4000 g and water washing, 16 nm Au NPs were trapped in the PNIPMAA spheres. By repeating incubation of the resultant composite spheres in the fresh Au NP dispersions, followed by consecutive centrifugation and washing with water, we can encapsulate as many as 230 Au NPs per PNIPMMA sphere after 5 incubations.

Mineralization of CaCO₃ within Au-PNIPMAA spheres. In-situ mineralization of CaCO₃ within Au-PNIPMAA was conducted based on the method reported elsewhere³. In glass vials, the Au-PNIPMAA spheres were well dispersed in a 10 mM CaCl₂ aqueous solution. The concentration of PNIPMMA was set as 1 wt%. The vials were put in a closed desiccator where solid (NH₄)₂CO₃ was used as the CO₂ vapour source. The crystallization of CaCO₃ resulted from the diffusion of CO₂. All mineralization experiments were carried out at room temperature. After 5 h mineralization, followed by filtration of the precipitates, the resulting dispersions were analyzed by DLS and SEM. After centrifugation at 4000g for 5 min to remove CaCO₃ – loaded Au-PNIPMAA spheres, Au@CaCO₃ NPs were obtained and suspended in the supernatants, which were imaged using TEM.

Formation of CaCO₃ nanocapsules. The resulting Au@CaCO₃ NPs were incubated within aqueous solutions of a mixture of KI and I₂ for 2 h.⁴ The weight ratio of KI to I₂ was 2:1 and the concentration of KI was 10 wt%. Triple centrifugation at 8000 g and washing with water and redispersion in water yielded CaCO₃ nanocapsules.

Characterization. DLS measurements were performed by using a commercial laser light scattering spectrometer (Malvern Autosizer3000) with a 5 mW He-Ne laser. TEM observations were performed on a Philips CM 120 electron microscope at an acceleration

voltage of 80 kV. For all TEM observations, the copper grids used were covered with a thin carbon film. Scanning electron microscopy (SEM) images were recorded by means of a Philips XL30 electron microscope at an accelerating voltage of 3 kV. The specimens were sputter-coated with gold before SEM imaging. XRD patterns were obtained by use of a PDS 120 diffractometer (Nonius GmbH, Solingen) with Cu-K α -radiation.

References:

1. *Colloidal Gold: Principles, Methods, and Applications* (Ed: M. A. Hayat), Academic Press: San Diego, CA, **1991**
2. Kuang, M.; Wang, D.; Möhwald, H. *Adv. Funct. Mater.* **2005**, *15*, 1611.
3. Kuang, M.; Wang, D.; Gao, M.; Hartmann, J.; Möhwald, H. *Chem. Mater.*, **2005**, *17*, 656.
4. Kumar, A.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1498.

Figure S1. SEM image of mixtures of CaCO_3 – loaded Au-PNIPMAA composite spheres and $\text{Au}@\text{CaCO}_3$ NPs (indicated by arrows), obtained from 5h mineralization of CaCO_3 within Au-PNIPMAA spheres.

Figure S2. XRD pattern of CaCO_3 nanocapsules, obtained by etching out Au cores of Au@CaCO_3 NPs that were formed by 5 h mineralization of CaCO_3 within Au-PNIPMAA spheres.