Supporting Information

Direct Growth of Optically Stable Gold Nanorods onto Polyelectrolyte Multilayered Capsules

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Figure S1. TEM images of (a) the PEM capsules and (b) the PEM-Silica capsules after reaction with preformed AuNRs for 12 hrs. There are little AuNRs attached on the capsule structure. The capsule diameter is 2 μm.
Supporting Experimental Section

Materials: Poly(styrene sulfonate) (PSS, Mw 70,000), poly(allylamine hydrochloride) (PAH, Mw 70,000), hydrogen tetrachloroaurate (HAuCl₄·3H₂O), cetyltrimethylammonium bromide (CTAB), silver nitrate (AgNO₃), sodium borohydride (NaBH₄), ascorbic acid (AA), sodium chloride (NaCl), hydrochloric acid (HCl), 2-propanol, tetraethylorthosilicate (TEOS, 99.9%), and ammonium hydroxide (NH₄OH) were purchased from Sigma-Aldrich. Weakly cross-linked MF particles were purchased from Microparticle (GmbH). Ultrapure deionized water was used for all solution preparations and experiments.

Preparation of PEM Capsules and PEM/Silica Capsules: 1.4 mL of a PSS solution (2 mg/mL) was added to 0.12 mL of an aqueous suspension of positively charged MF particles (10 wt %, 1.8 μm and 5 wt %, 590 nm). The dispersion was vigorously agitated by shaking for 15 min to allow the polyelectrolyte to adsorb onto the MF particles. The resulting dispersion was centrifuged at 10,000 g for 3 min; subsequently, the supernatant was removed and 1.4 mL of water was added. The centrifugation/washing/dispersion cycles were repeated three times. After the formation of a PSS layer on the MF cores, PAH (1.4 mL of a 2 mg/mL solution) layers were deposited using the LbL assembly technique. The adsorption and rinsing steps were repeated until the desired number of layers was obtained. In total, nine polyelectrolyte multilayers were deposited on the MF particles. Finally, PEM capsules were obtained by decomposing MF cores with 0.15 M HCl solution (pH < 1). For silica coating onto PEM capsules (PEM-Silica capsules), the PEM capsules were dispersed in a
solution containing 1 mL of 2-propanol, 0.18 mL of water, and 0.025 mL of NH$_4$OH. The resulting
solution was stirred vigorously for 30 min after the addition of 30 µL tetraethylorthosilicate (TEOS),
which resulted in the formation of silica shell with thickness of 50 nm outside the PEM capsules.
The thickness of the silica shell can be controlled by amount of TEOS and reaction time for silica
growth.

*Synthesis of Gold seeds:* Gold seeds and nanorods were prepared using a wet-chemical method
similar to the method described by Sau et al. In a typical procedure, 0.25 mL of an aqueous 0.01 M
solution of HAuCl$_4$·3H$_2$O was added to 7.5 mL of a 0.10 M CTAB solution in a test tube. The
solution gently mixed by the inversion appeared bright brown-yellow in color. Then, 0.60 mL of an
aqueous 0.01 M ice-cold NaBH$_4$ solution was added all at once, followed by rapid inversion mixing
for 2 min. This seed solution was kept at 25°C and was used 2 h after its preparation for further
growth of gold nanorod.

*Gold Nanorod Growth on PEM capsules or PEM-Silica capsules:* In a typical experiment, 4.75 mL
of 0.10 M CTAB, 0.20 mL of 0.01 M HAuCl$_4$·3H$_2$O, and 0.03 mL of 0.01 M AgNO$_3$ solutions were
added in that order, one by one, to a test tube, followed by gentle mixing by inversion. (Aspect ratio
of the AuNRs was controlled by the amount of the AgNO$_3$ added in the growth solution.) The
solution at this stage appeared bright brown-yellow in color. Then 0.032 mL of 0.10 M AA was
added to it. The solution became colorless upon addition and mixing of AA. Finally, 0.1 mL of the
PEM capsules or PEM/Silica capsules (0.01 wt %) and 0.01 mL of seed solution were added, and the reaction mixture was gently mixed for 10 s and left undisturbed for at least 3 h.

**Characterization**: Absorption spectra of the capsules containing gold nanorods were taken on a Cary 1E (Varian) scan UV-vis-NIR spectrophotometer. FE-TEM measurements were performed on a Philips (Tecnai F20) microscope operating at 200 kV. A drop of sample solution was spread on a carbon coated copper grid and dried overnight at room temperature. The surface charge potentials of the CTAB-capped PEM capsules and PEM-Silica capsules were measured by streaming potential measurement system (ESA 9800, Matec).