Supplementary Information

Highly Monodisperse Rattle-Structured Nanomaterials with Gold Nanorod Core/Mesoporous Silica Shell as Drug Delivery Vehicles and Nanoreactors

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Experimental section

Chemicals. Cetyltrimethylammonium bromide (CTAB, 95%), sodium borohydride ($NaBH_4$, ≥98.0%), gold(III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, ≥99.9%), silver nitrate ($AgNO_3$, 99.999%), L-ascorbic acid (AA, ≥99%), and doxorubicin hydrochloride (DOX, ≥98.0%) were all obtained from Sigma-Aldrich. Sodium hydroxide (NaOH), tetraethyl orthosilicate (TEOS, 98.0%), and hydrogen peroxide (H_2O_2, 30.0–35.5% (SG)) were purchased from Samchun. Ultrapure deionized water was used for all solution preparations and experiments.

Preparation of Au nanorods. Gold nanorods (AuNRs) were synthesized using a seed-mediated growth method with slight modifications according to the report by Murphy et al.[s1] As in a typical synthesis procedure, the seed solution was prepared by adding 600 μL of ice-

cold 0.01 M $NaBH_4$ to an aqueous solution containing 250 μL of 0.01 M $HAuCl_4 \cdot 3H_2O$ and 7.5 mL of 0.1 M CTAB under vigorous stirring. The color of the solution immediately changed from yellow to brown, indicating the formation of gold nanoparticle seeds. The solution was constantly stirred for 2 h. For the growth of seeds, an aqueous growth solution containing 9.5 mL of 0.1 M CTAB, 400 μL of 0.01 M $HAuCl_4 \cdot 3H_2O$, 60 μL of 0.01 M $AgNO_3$, and 64 μL of 0.1 M AA was prepared. AuNRs were grown by adding 10 μL of the seed solution to the growth solution and leaving this mixture overnight.

Synthesis of AuNR@Ag core/shell nanoparticles. Silver-coated AuNRs were prepared using a modified procedure proposed by Xie et al.[s2] 20 μL of 0.1 M AA and 1 mL of 0.01 M $AgNO_3$ were mixed with 6 mL of as-prepared Au NRs. 300 μL of 0.1 M NaOH was then added to this mixture to increase the pH to 10 because AA could reduce silver ions only in a basic medium.[s3] The mixture was vigorously stirred for 2 h to ensure complete coating of silver.

Synthesis of AuNR@Ag@mSiO$_2$ core/shell/shell nanoparticles. CTAB-stabilized AuNR@Ag nanoparticles were coated with mesoporous silica shells through the Stöber method. For this purpose, a slightly modified version of the procedure described by Matsuura et al. was employed.[s4] 5 mL of an as-prepared AuNR@Ag colloid solution was mixed with 25 μL of 0.1 M NaOH under stirring. Thereafter, 30 μL of TEOS dispersed in methanol (10% v/v) was added at 1 h intervals for 3 h under gentle stirring. The reaction was allowed to proceed for 24 h at room temperature.

Synthesis of rattle-structured AuNR@mSiO$_2$ core/void/shell nanoparticles. We used H_2O_2 for removing silver. Silver can be selectively etched by H_2O_2 because the standard redox potential of H_2O_2 is more positive than that of silver.[s5] Under magnetic stirring, 8 mL of H_2O_2 was added to 4 mL of a AuNR@Ag@$mSiO_2$ solution, and the mixture was left undisturbed for over 12 h. The obtained rattle-structured AuNR@$mSiO_2$ nanoparticles were then centrifuged and washed with ethanol at least twice and redispersed in ethanol (4 mL).

Loading of DOX. 3 mL of a solution containing rattle-structured AuNR@$mSiO_2$ nanoparticles was centrifuged and dispersed in 1 mL of DI water. The solution was mixed with 300 μL of an aqueous DOX solution (0.2 mg/mL). After stirring for 24 h in the dark, the DOX-loaded nanocapsules were precipitated through centrifugation at 15,000 rpm for 5 min.

To evaluate the DOX-loading efficiency, the contents of the original and residual DOX solution in the supernatant were determined by UV–Vis measurements at 490 nm. The loading efficiency (LE%) of DOX can be calculated as follows: LE% = $[(O_{DOX} - R_{DOX})/O_{DOX})] \times 100\%$, where O_{DOX} and R_{DOX} are the contents of the original and residual DOX solution, respectively.

Regrowth of gold within rattle-structured AuNR@mSiO$_2$. Three sets of as-prepared rattle-structured AuNR@mSiO_2 (200 μL) solutions were mixed with 800 μL of DI water containing a 10 mM $HAuCl_4$ solution in different concentrations (3 μL, 15 μL, and 60 μL) under stirring to obtain three different samples. In these three samples, 24 μL (6 μL/min), 120μL (12 μL/min), and 480 μL (12 μL/min) of 5 mM AA were respectively injected.

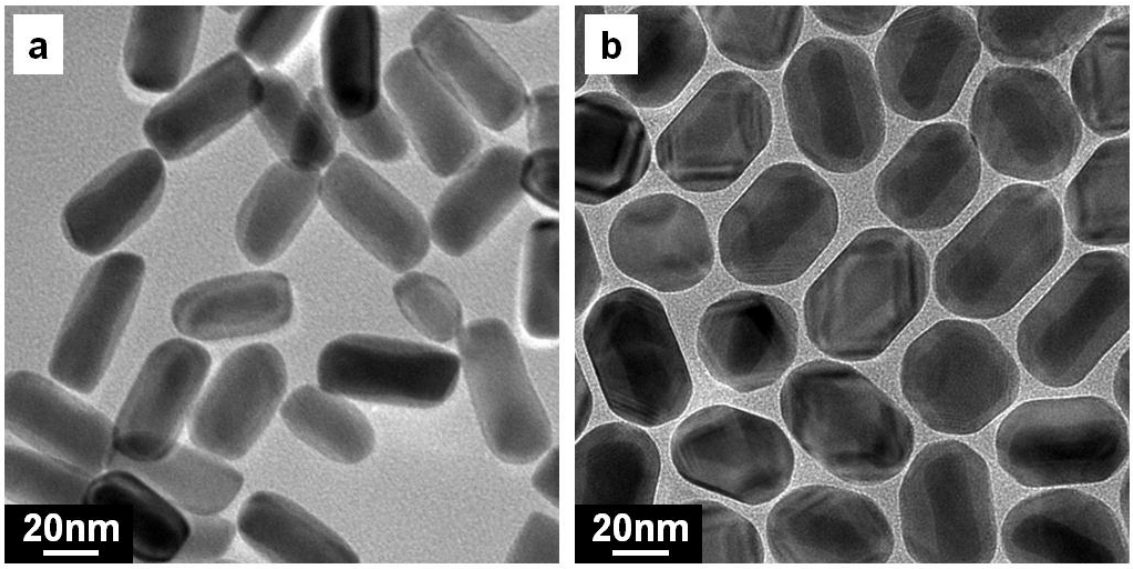

Fig. S1 TEM images of AuNR@Ag nanoparticles with different silver shell thicknesses. The surfaces of AuNRs were coated with silver shells having thicknesses of (a) 5 nm and (b) 11 nm, obtained by adjusting the amount of $AgNO_3$ to 0.001 mmol and 0.01 mmol, respectively.

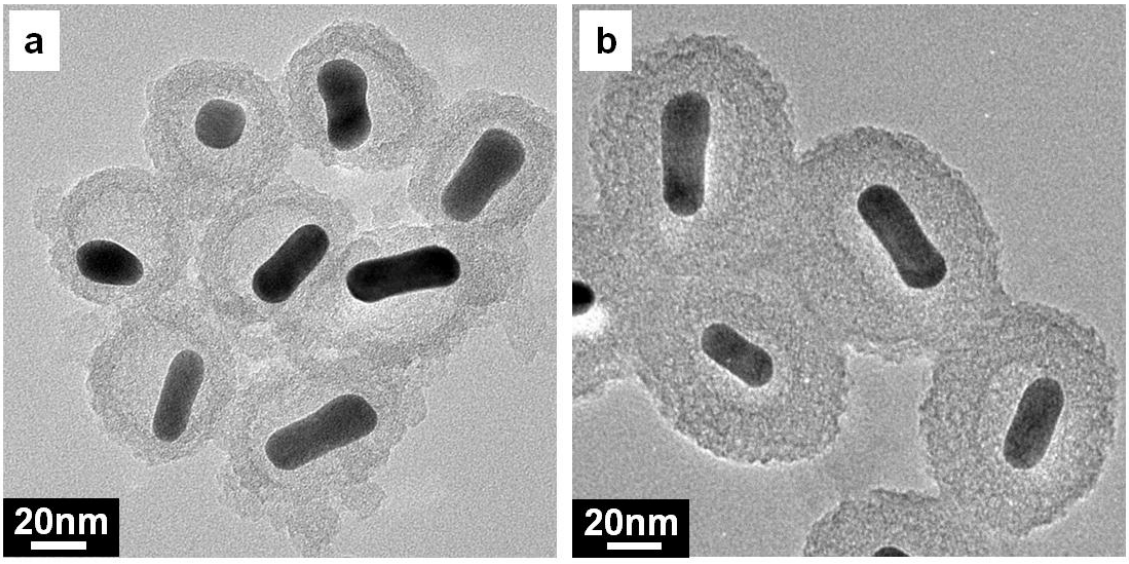

Fig. S2 TEM images of rattle-structured AuNR@mSiO_2 with different SiO_2 thicknesses. The shell thicknesses of (a) 8 nm and (b) 21 nm were obtained at TEOS concentrations of 0.04 mmol and 0.08 mmol, respectively.

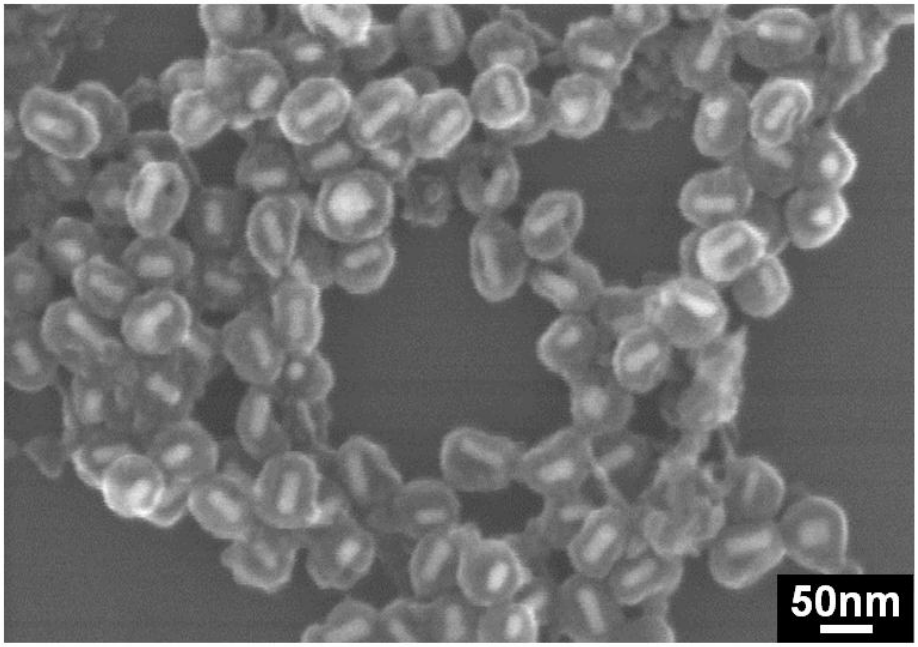

Fig. S3 SEM image of rattle-structured AuNR@mSiO_2.

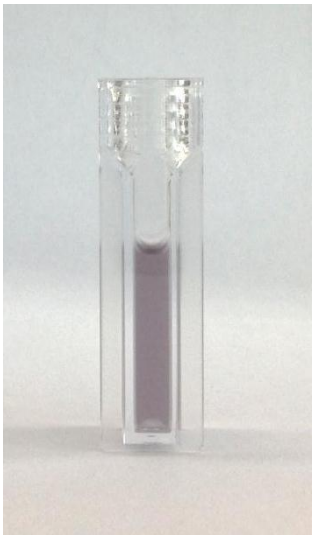

Fig. S4 Photograph of the rattle-structured AuNR@SiO_2 dispersed in aqueous solution.

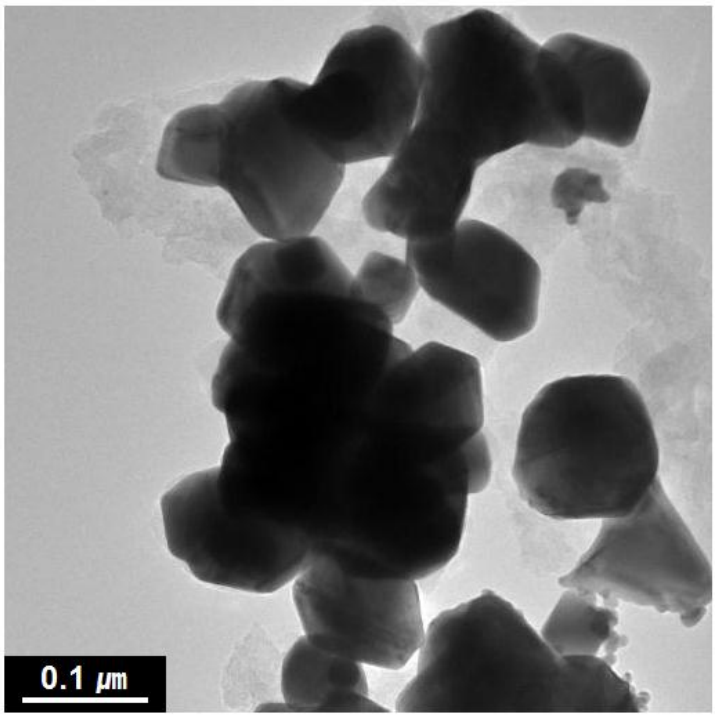

Fig. S5 TEM image of nanoparticles regrown from AuNRs without silica nanocapsules.

References

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