Supplementary Information

Designing anisotropic inorganic nanocapsules via self-assembly of polymer-like ultrathin Au nanowires

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EXPERIMENTAL SECTION

Materials

All chemicals were used without further purification. Au (III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$) was purchased from Sigma Aldrich. Oleylamine (OAm) was purchased from J&K Scientific Co., Ltd. (Beijing, China). Triisopropylsilane (TIPS) was purchased from Alfa Aesar. Other chemicals were purchased from Xilong Chemical Co., Ltd. (Shantou, China).

Preparation of ultrathin Au NWs

Ultrathin Au NWs (Au NWs) were prepared following a previously reported method.[1] First, 3 mg of $HAuCl_4 \cdot 3H_2O$ was dissolved in 2.5 mL tetrahydrofuran (THF). Then 100 μL of oleylamine (OAm) was added to form a yellow mixture, followed by adding 150 μL of triisopropylsilane (TIPs). The mixed solution was incubated at room temperature for 5 h. The color of the solution changed from yellow to dark brown, demonstrating the successful production of long ultrathin Au NWs. The as-synthesized ultrathin Au NWs were purified by centrifugation and redispersed in the THF for further use.

Assembly of Au NWs

300 μL of ethanol purified NWs were redissolved in 400 μL of THF. Then 1 mL of 8 mM sodium dodecyl sulfate (SDS) solution was quickly injected under vigorous stirring. The mixture was heated at 60 ℃ for 2 h without sealing to remove THF. The as-synthesized Au nanocapsules were purified by centrifugation and redispersed in the deionized water for further use. Au nanorings were prepared by the same method except using 200 μL as-synthesized Au NWs.

Incorporation of pyrene into Au nanocapsules

During the assembly process of nanocapsules, 30 μl pyrene (10 mg/mL) was added. After the assembly, the obtained nanocapsules with pyrene loaded were washed by H_2O (centrifugated at

1000 rpm for 5 minutes) 3 times in order to remove the extra pyrene and surfactant. Then the nanocapsules were dissolved in 1 mL H_2O.

Quantification of the pyrene loaded by Au nanocapsules

First, certain amount of Au nanocapsules with pyrene was incubated in a DMF solution (1 mL) at 80 ℃ for 4 h. This solution was then centrifuged to remove the nanomaterials. The pyrene loading was quantified by a standard curve based on UV/Vis spectra. The absorbance of pyrene loaded Au nanocapsules at 339 nm was 1.7641.

Fluorescence measurements of the pyrene release

The pyrene-loaded Au nanocapsules (30 μL) were added to different release media (4 mL), namely, H_2O, 0.3% SDS (in PBS; pH 5.5), 0.3% SDS (in PBS; pH 7.4). For all measurements the emission intensity at 395 nm was recorded every two minutes at an excitation wavelength of 334 nm. The excitation and emission slits were kept at 5 nm.

Characterization

Scanning electron microscope (SEM) images were obtained on SU-70 with the accelerating voltage of 10 kV. Transmission electron microscope (TEM) images were taken from JEM-1400 operated at 100 kV. Viscosity curve was measured from an Anton Paar MCR302 rotational rheometer using CP25-2-SN rotor and gap=0.10 mm. Samples were all at a concentration of 3mg/mL. In the kinetic experiments, the fluorescence was measured on Fluoromax-4 in a cuvette of 1 cm pathlength. The excitation and emission slits were kept at 5 nm; and the excitation wavelength was at 334 nm.

SUPPLEMENTARY FIGURES

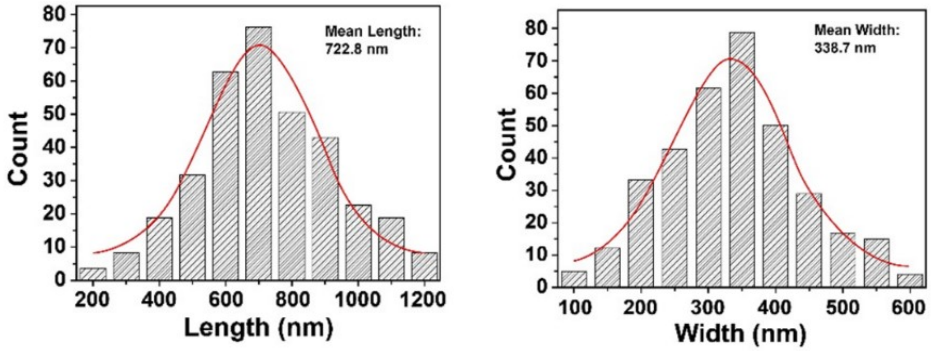

Figure S1. The size distributions of Au nanocapsules.

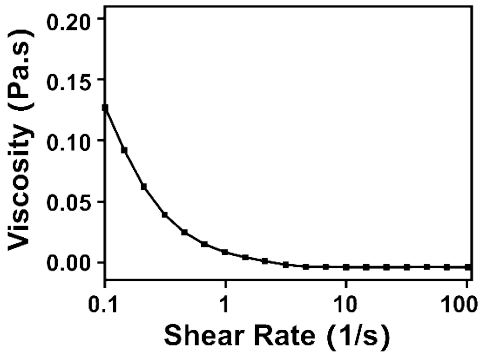

Figure S2. Viscosity versus shear rate of Au nanocapsules.

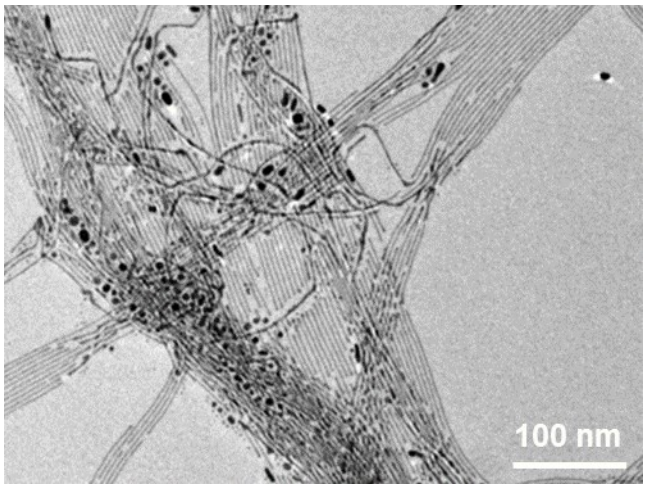

Figure S3. The nanoparticles found in the prepared nanowires.

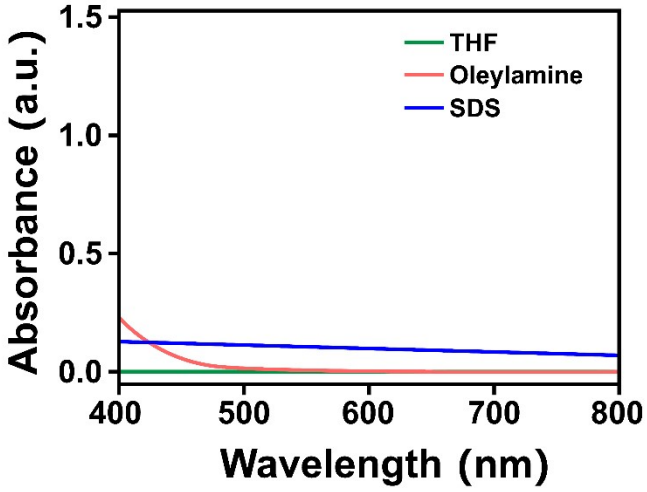

Figure S4. UV−vis spectra of THF, oleylamine and SDS.

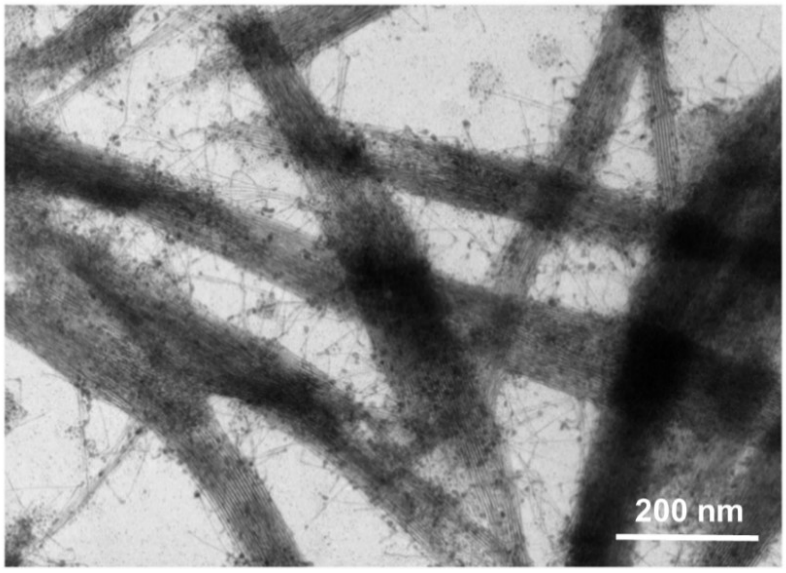

Figure S5. TEM image of bunched secondary structure assembled by Au NWs.

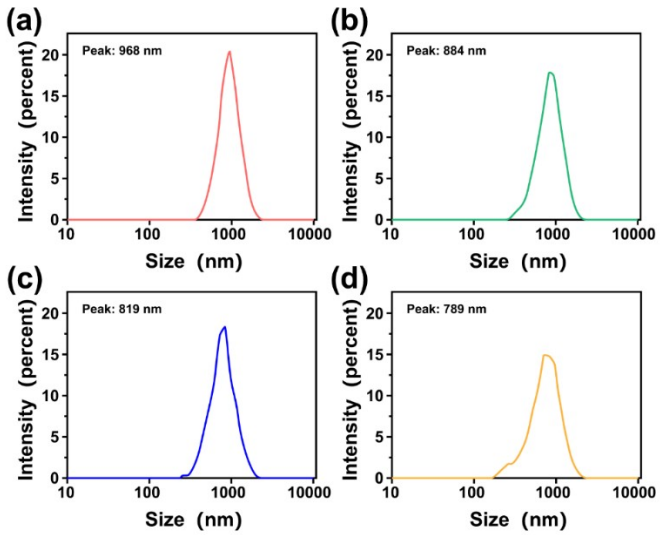

Figure S6. At different moments of the assembly process, the nanowires were collected, and the sizes of the assemblies were measured. The four figures show particle size distribution measurements at (a) 30 min, (b) 60 min, (c) 90 min and (d) 120 min, respectively.

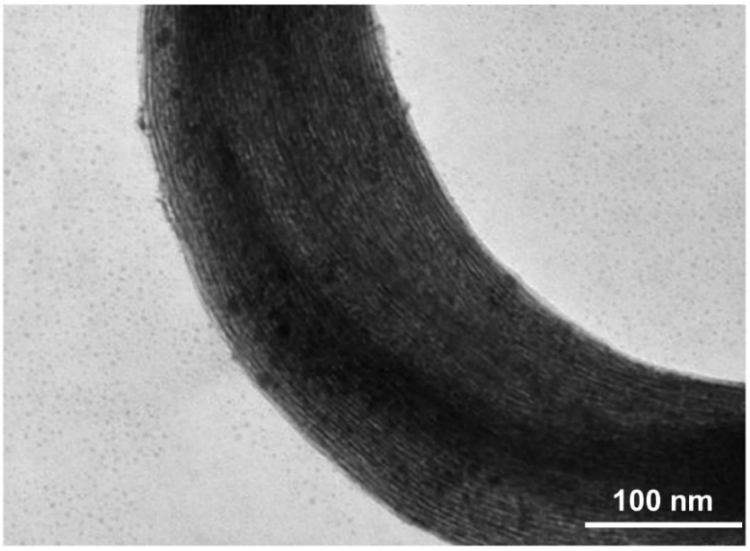

Figure S7. TEM image of the nanorings assembled by parallel Au nanowires.

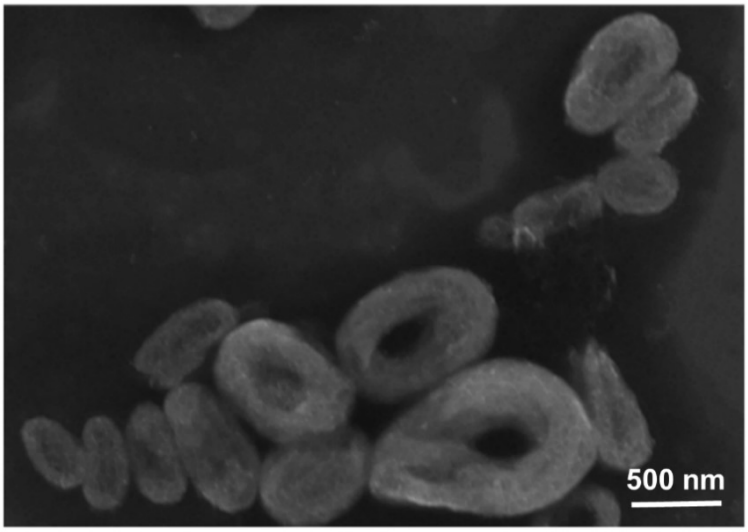

Figure S8. TEM image of the products assembled by Au NWs with high THF content after heating for 4 h.

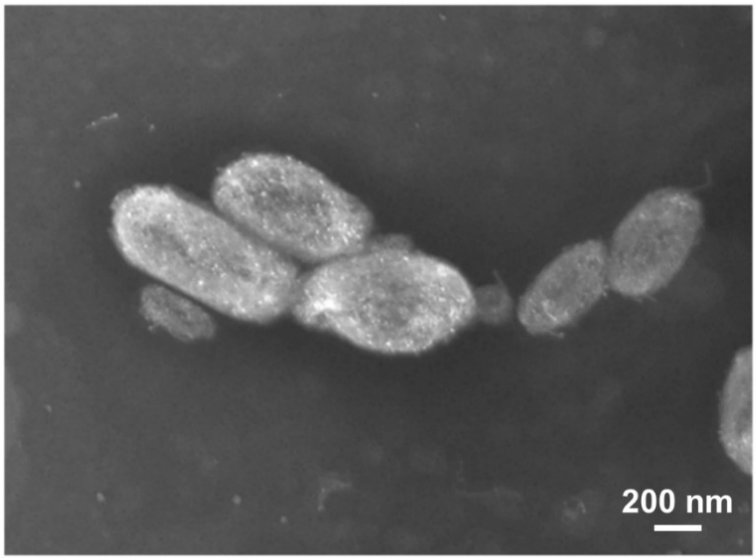

Figure S9. SEM image of Au nanocapsules loaded with pyrene.

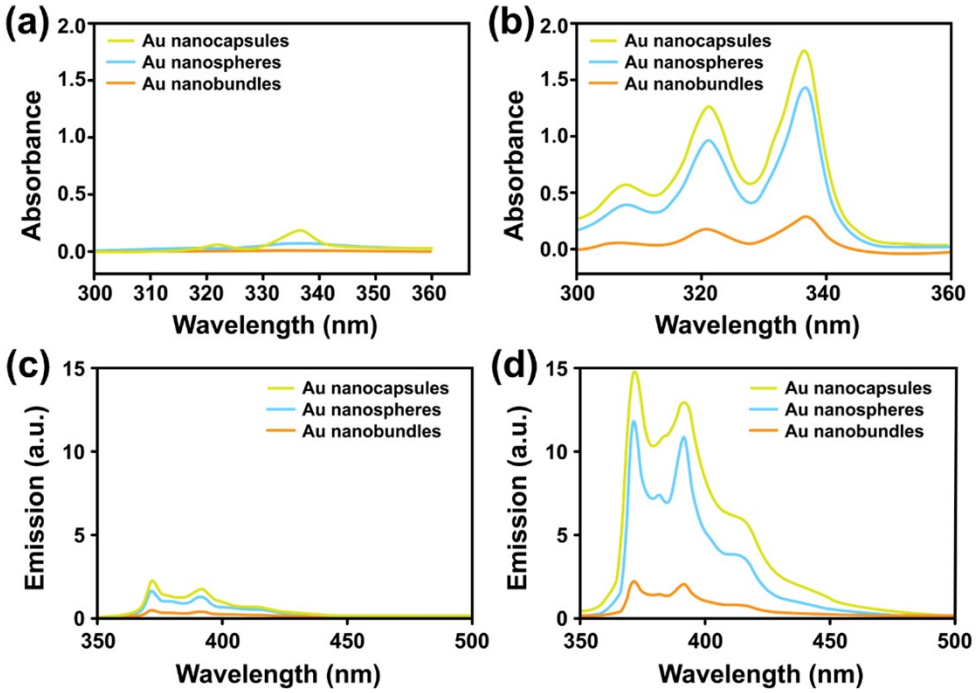

Figure S10. Ultraviolet absorption spectra of the DMF solution of pyrene loaded three carriers (a) before and (b) after release. Fluorescence emission spectra of the DMF solution of pyrene loaded three carriers (c) before and (d) after release.

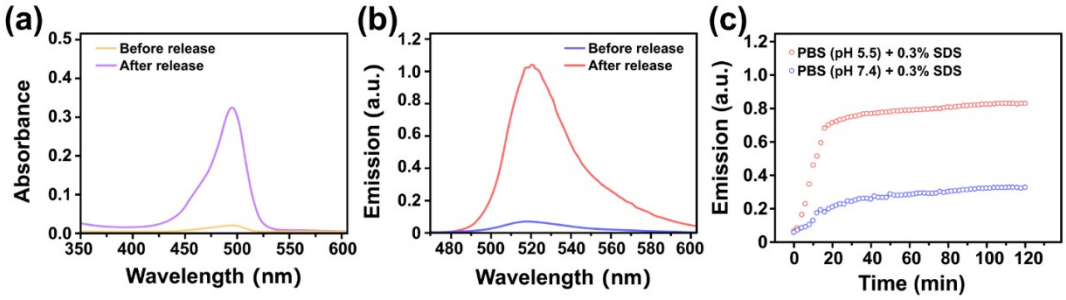

Figure S11. (a) Ultraviolet absorption spectra and (b) fluorescence emission spectra of the DMF solution of Rhodamine 110 loaded Au nanocapsules before and after release. (c) The release curve of Rhodamine 110 loaded Au nanocapsules in PBS with different pH.

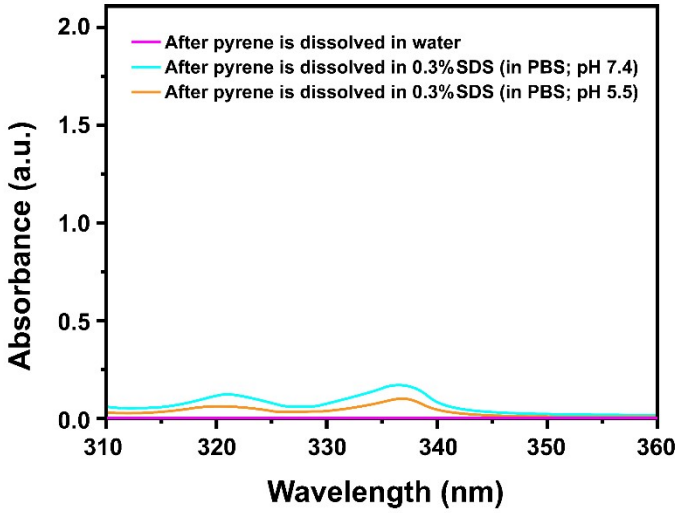

Figure S12. Solubility of pyrene under different conditions.

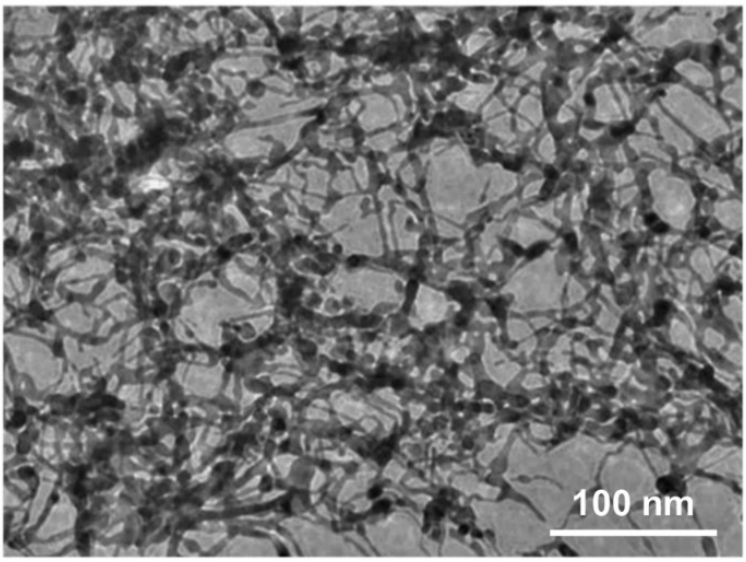

Figure S13. TEM image of Au nanocapsules after release in SDS solution with pH=5.5.

Table S1. The influences of four factors on the morphology.

Regulatory Factors		Forces			Morphologies
		Interfacial Tension	Molecular Force	Strain Force	
Au NWs concentration	Low	-	↓	↓	Nanorings
	High	-	↑	↑	Nanobundles
THF concentration	Low	↑	-	-	Deformed nanobundles
	High	↓	-	-	Transition states between nanotubes to nanocapsules
Oleylamine concentration	None	↑	↓	-	Scattered NWs
	High	↓	↑	-	Nanobundles with oil droplets inside
Temperature	No heating, short time	↓	↓	-	Nanobundles and a few loose nanorings
	No heating, long time (2 h)	↓	↓	-	Transition states between loose nanotubes to nanocapsules

Table S2. The diffusion kinetic fitting results in Figure 4d.

Model	Equation*	PBS (pH 7.4) + 0.3% SDS		PBS (pH 5.5) + 0.3% SDS	
		k	Correlation coefficient (R)	k	Correlation coefficient (R)
Zero-order	$Q=Q_0+kt$	0.019±0.002	0.7147	0.026±0.004	0.4651
First-order	$Q/Q_0=1-e^{-kt}$	0.048±0.002	0.9698	0.134±0.009	0.9396
Higuchi	$Q=kt^{1/2}$	0.71±0.02	0.2135	1.22±0.04	0.2301
Ritger-Peppas	$Q=kt^{n}$	3.31±0.14	0.8119	6.50±0.19	0.8956
Hixson-Crowell	$Q^{1/3}-Q_0^{1/3}= kt$	0.31±0.02	0.1844	0.56±0.03	0.3409

*Q represents the amount of drug released at time t; Q_0 is the initial amount of drug; k is the release constant.

References

1. H. Feng, Y. Yang, Y. You, G. Li, J. Guo, T. Yu, Z. Shen, T. Wu and B. Xing, *Chemical Communications*, 2009, 1984-1986.