

Materials and measurements

All materials and reagents were obtained from commercial suppliers for direct use unless mentioned. TEM observations were performed on a Philips CM 120 electron microscope at an accelerating voltage of 80 kV. A small drop from the solution was deposited onto carbon-coated copper grid and then dried at room temperature. UV/Vis spectra were recorded on a Perkin-Elmer Lambda 35 UV/Vis spectrophotometer. ^1H NMR (400 MHz) and ^{13}C NMR (400 MHz) spectra were recorded by using a JOEL ECA-400 instrument.

Terminal amino calix[6]crowns (TAC) was synthesized according to the procedure of our reference (Soft matter, 2008, 4, 1393). Solutions of HAuCl_4 or AgNO_3 were injected into TAC ethanol solution under stirring for the preparation of the nanohybrids. After then, the solution of NaBH_4 needed was dropwise added to the system, and the color of the resultant solution changed. The mixture was stirred for 1 h and finally, precipitates were formed in the solution. The droplet of the solution was deposited on a copper grid for the sample of transmission electron microscopy (TEM). X-ray diffraction (XRD) spectra were registered with a Philips diffractometer composed of a $\text{CuK}\alpha$ ($\lambda = 1.54 \text{ \AA}$) source, a quartz monochromator, and a goniometric plate.

The liquid phase catalytic hydrogenation of crotonaldehyde (CRAL) was conducted in a 100 mL quartz-lined stainless steel autoclave with a thermocouple and magnetic stirring device coupled with a magnetic stirrer. The catalyst (containing variable amount of metal NPs), 0.1 mL CRAL and 20 mL solvent (H_2O) were added to the reactor. The reaction vessel was sealed and purged 6 times with pure hydrogen. After the required temperature (373 K) was reached, the rotation rate of stirrer was adjusted at 1000 rpm and the H_2 pressure was raised to 2 MPa. This time point was deemed as the commencement of the hydrogenation reaction.

The progress of the reaction was monitored by sampling a certain amount of microsample at appropriate intervals and analyzing them on a gas chromatograph (GC Trace Ultra) equipped with XE-60 capillary column ($30 \text{ m} \times 0.32 \text{ mm}$) and a flame ionization detector (FID).

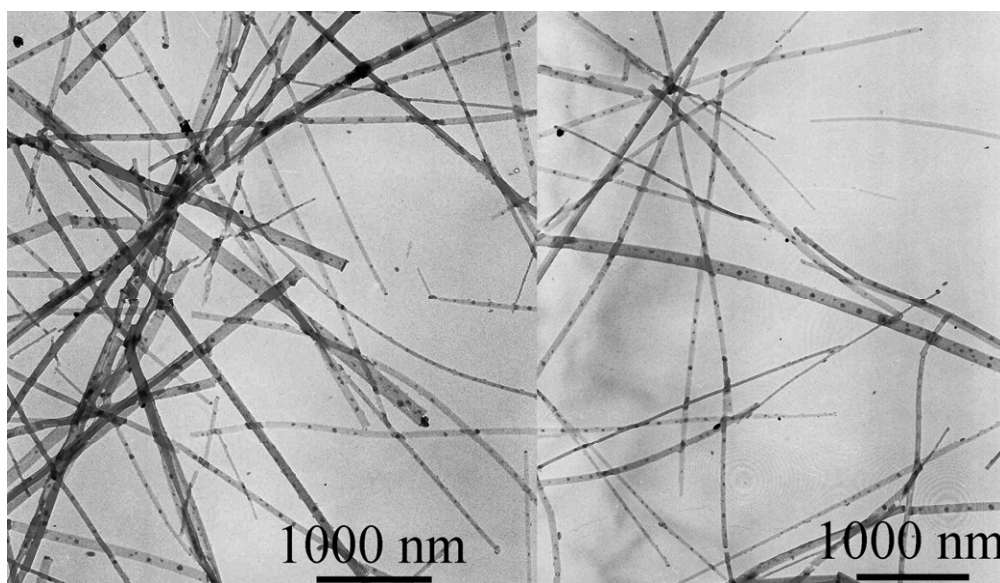


Figure S1. TEM image of TAC nanotubes with gold particles without chemical reduction (the concentration of HAuCl_4 was 0.5 mg/mL)

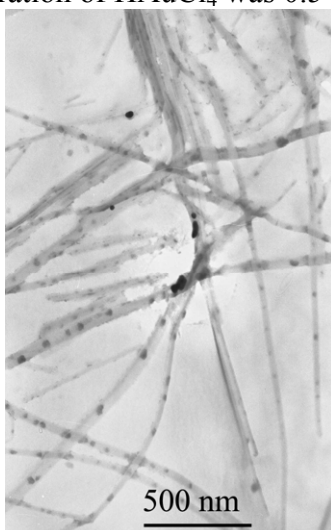


Figure S2. TEM image of TAC aggregates with gold particles without chemical reduction after energy dispersive X-ray (EDX) analysis (the concentration of HAuCl_4 was 0.5 mg/mL).

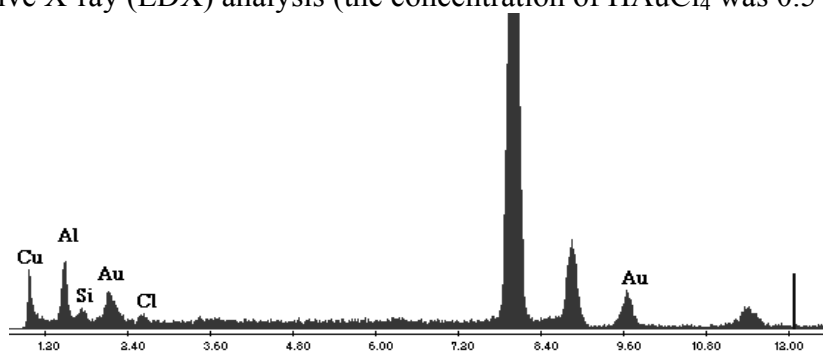


Figure S3. EDX spectra of TAC nanotubes with gold particles without chemical reduction
(the concentration of HAuCl_4 was 0.5 mg/mL).

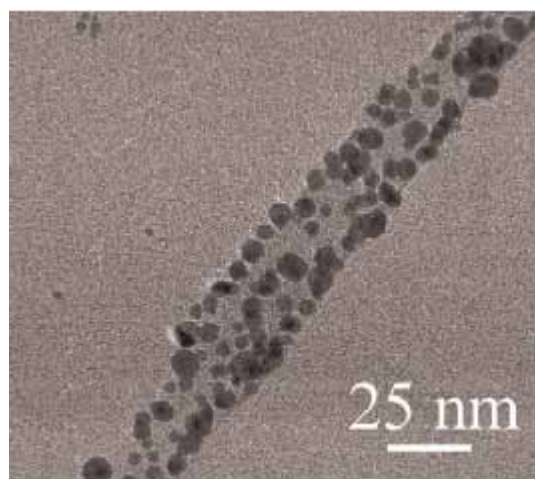


Figure S4. HR-TEM image of hybrids H3

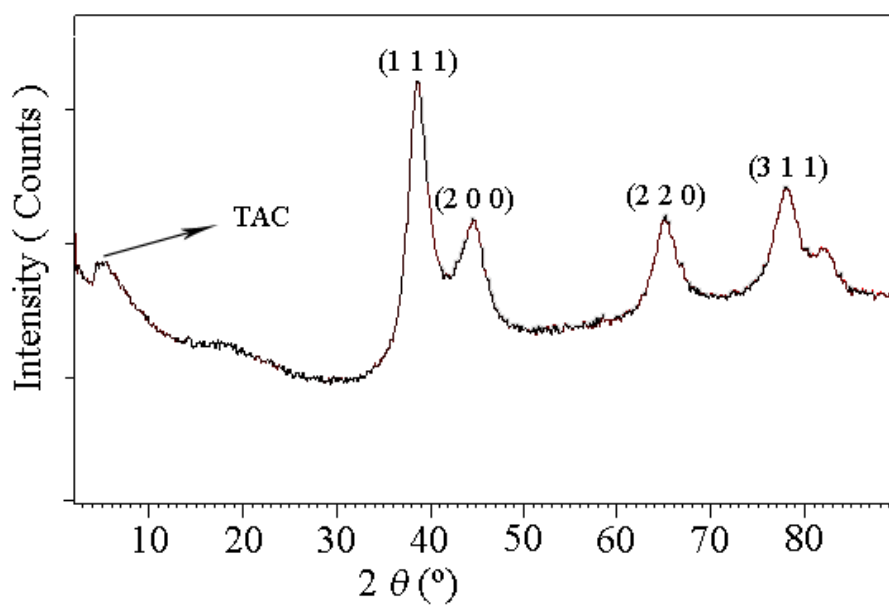


Figure S5. XRD spectrum of hybrids H3

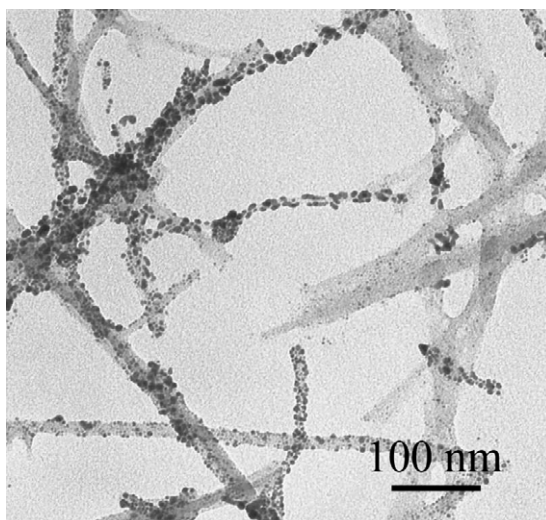


Figure S6. TEM image of hybrids H4

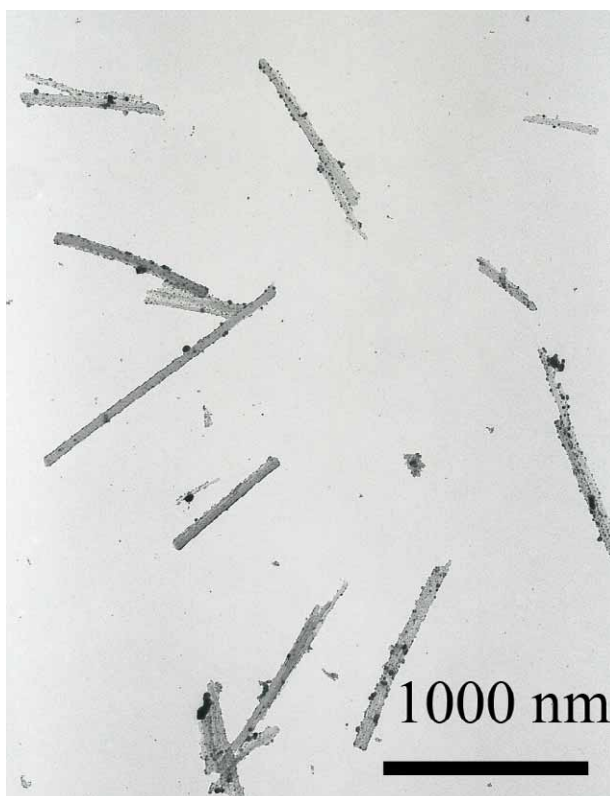


Figure S7. TEM image of hybrids H4 after ultrasonic treatment

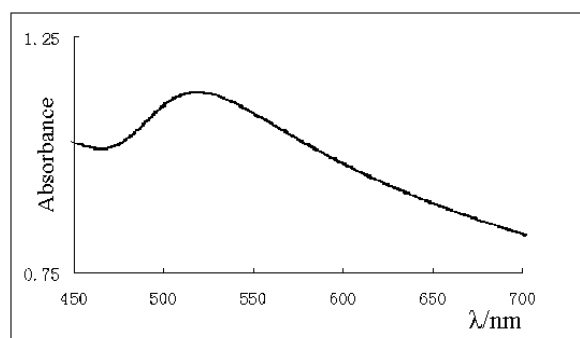


Figure S8. UV-vis spectra of the hybrids prepared with concentration of HAuCl_4 2.5 mg/mL.

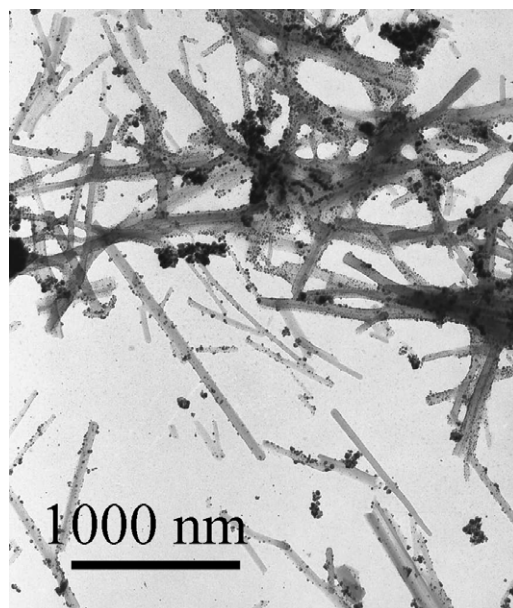


Figure S9. TEM image of hybrids with concentration of HAuCl_4 2.5 mg/mL.

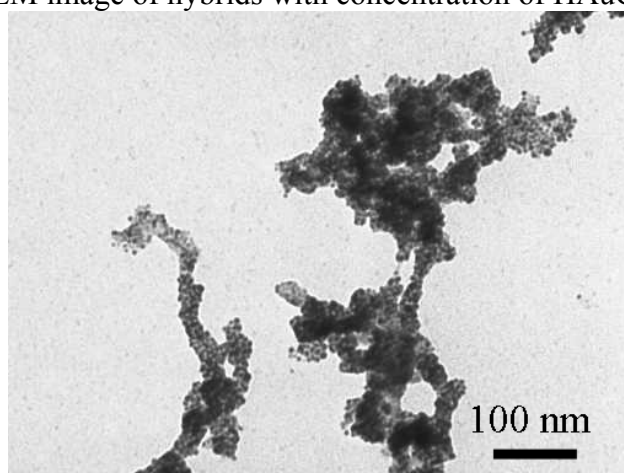


Figure S10. TEM image of the hybrids with concentration of HAuCl_4 2.5mg/mL after the hydrogenation reaction

Reaction time (h)	CRAL	CROL	BUAL	BUOL	Conversion	Selectivity For CROL	Selectivity for BUAL
10	75.53%	1.23%	20.57%	2.68%	24.47%	5.023%	84.03%
20	54.37%	1.18%	40.90%	3.54%	45.63%	2.59%	89.65%
33	40.74%	1.53%	50.72%	7.02%	59.26%	2.58%	85.57%
45	30.85%	2.34%	54.75%	12.06%	69.15%	3.38%	79.18%
61	17.02%	2.00%	64.09%	16.89%	82.98%	2.41%	77.24%
84	5.51%	2.03%	64.81%	27.65%	94.49%	2.15%	68.59%

Table S1. The result of the hydrogenation of TAC nanotubes with gold NPs (the concentration of HAuCl_4 was 1 mg/mL, and the weight mount of gold NPs was approximately 2.5 mg)

Reaction time (h)	CRAL	CROL	BUAL	BUOL	Conversion	Selectivity for CROL	Selectivity for BUAL
12	51.56%	14.00%	19.94%	14.50%	48.44%	28.90%	41.16%
22	16.80%	18.38%	28.71%	36.11%	83.30%	22.09%	34.51%
32	0.00%	17.87%	16.34%	65.79%	100.00%	17.87%	16.34%

Table S2. The result of the hydrogenation of TAC nanotubes with gold NPs (the concentration of HAuCl_4 was 5 mg/mL, and the weight mount of gold NPs was approximately 7.5 mg)