Supplementary Material (ESI) for Chemical Communications



# Supporting Information

# Temperature-dependent Synthesis of CoPt Hollow Nanoparticles: from "Nanochain" to "Nanoring"

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## Experimental Section

**Reagents** Cobalt chloride, trisodium citrate dehydrate, $H_2PtCl_6$ were purchased from Beijing chemical reagent Ltd and used without further treatment. Sodium borohydride ($NaBH_4$, 99%) was purchased from Aldrich. All chemicals were of analytical reagent grade and used as received. Water used for preparation of aqueous solutions was purified using a Millipore-Q water purification system.

### Synthesis of different assembly morphological CoPt hollow nanospheres

The chain-like CoPt hollow nanoparticles were synthesized following the procedure developed by Vasquez et al[1] with some changing. Briefly, 50 mL of double-distilled $H_2O$ contain $CoCl_2.6H_2O$ (0.7 mM) and trisodium citrate dehydrate (0.7 mM) was purged with $N_2$ for 30 min, and the solution was kept at different temperature by a water bath. A freshly prepared solution of $NaBH_4$ (20 mL, 13mM) was then added quickly under mechanical stirring. After all of the $NaBH_4$ has been added, $H_2PtCl_6$ (20 ml, 2 mM) was added immediately. To avoid the oxidation of Co nanoparticles in the presence of atmospheric oxygen, $N_2$ is bubbled through the solution during the whole procedure. After 30 min, the product was collected by centrifugation, washed for several times. The monodisperse CoPt hollow nanoparticles were synthesized by the same procedure at 35 °C except that 40mg trisodium citrate dehydrate was used.

### Synthesis of Citrate-Stabilized Pt nanoparticles

Pt nanoparticles were synthesized following the reported procedures.[2] 1 mL of 1% $H_2PtCl_6$ aqueous solution was added into 100 mL of $H_2O$ and then heated to boiling. 3 mL of 1% sodium citrate aqueous solution was added rapidly, and the mixture was kept at a boiling temperature for 30 min. The product was collected by centrifugation, washed for several times.

### Instrumentation

Samples for TEM were prepared by placing a drop of solution onto a carbon-coated copper grid and examined using a JEOL 2010 transmission electron microscope operated at 200 kV. X-ray photoelectron spectroscopy (XPS) measurement was performed on an ESCALAB-MKII spectrometer

(VG Co.) with $Al_{K\alpha}$ (X-ray radiation as the X-ray source for excitation and analyzer pass energy of 50 eV). Typically, the operating pressure in the analysis chamber was below $10^{-9}$ Torr. The resolution of the spectrometer was 0.2 eV. XPS measurement was performed on a Si slide with several drops of aqueous solution of the samples. A XL30E SEM scanning electron microscope equipped with an energy-dispersive X-ray (EDX) analyzer was used to determine the composition of the products.

**Electrochemical Measurements**

Electrochemical experiments were performed with a CHI 660 electrochemical workstation at room temperature in a home made electrochemical cell. A microscope glass slide ( 3.75 cm × 2.50 cm × 0.10 cm) coated with a 200-nm-thick gold layer was firstly placed on a magnet, then a piece of poly-dimethylsiloxan (PDMS) with inset of a piece of glass carbon ( 1.0 cm × 1.0 cm × 0.2 cm) was put on the surface of the gold. Another piece of PDMS with a hole (d = 3 mm) laid above was used to determine the surface area of the electrode. A vessel with a hole was placed on the top of the PDMS and used to accommodate the electrolyte. The catalysts were dispersed in water, and the suspension was deposited on the surface of glass carbon, attracted by a magnet. The solution was moved away carefully from the electrode surface after 5 min. The auxiliary electrode and reference electrode were made of a twisted platinum wire and Ag/AgCl wire, respectively.

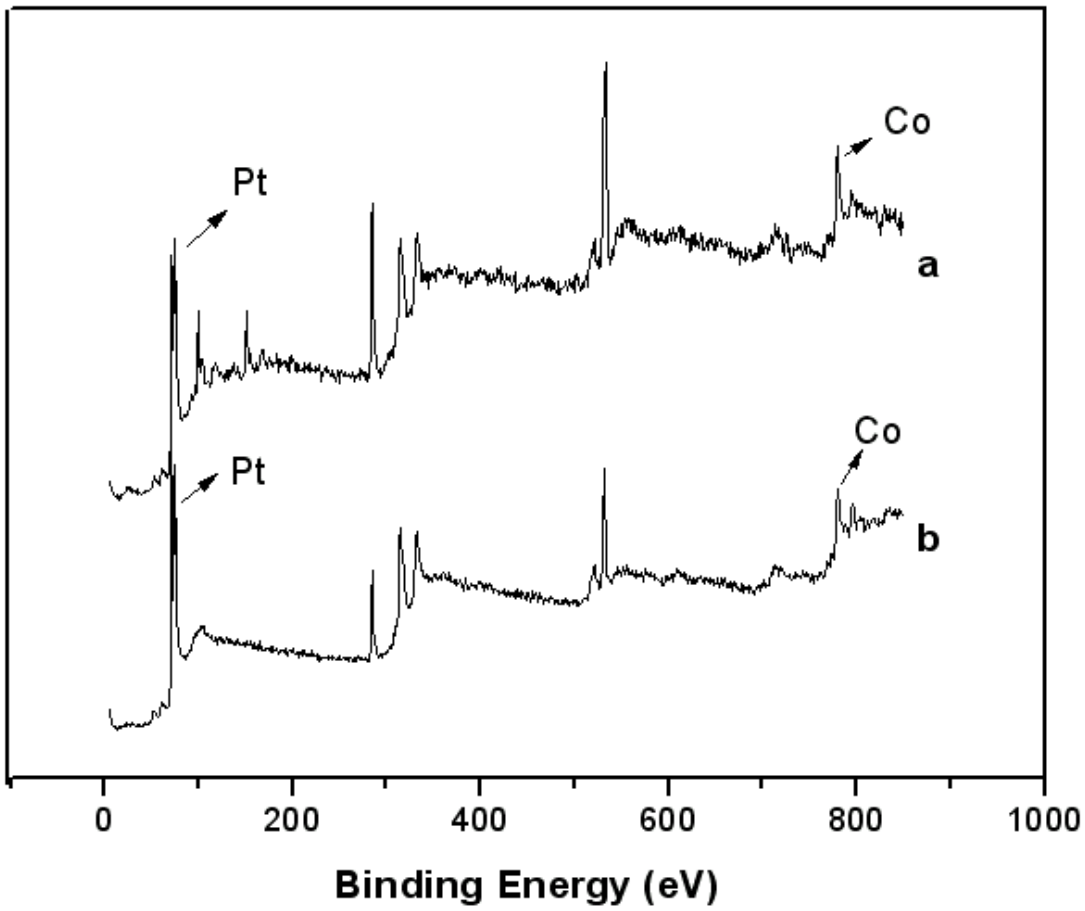


**Fig.S1** XPS spectrum of the chain-like CoPt hollow nanoparticles (a) and the ring-like CoPt hollow nanoparticles (b).

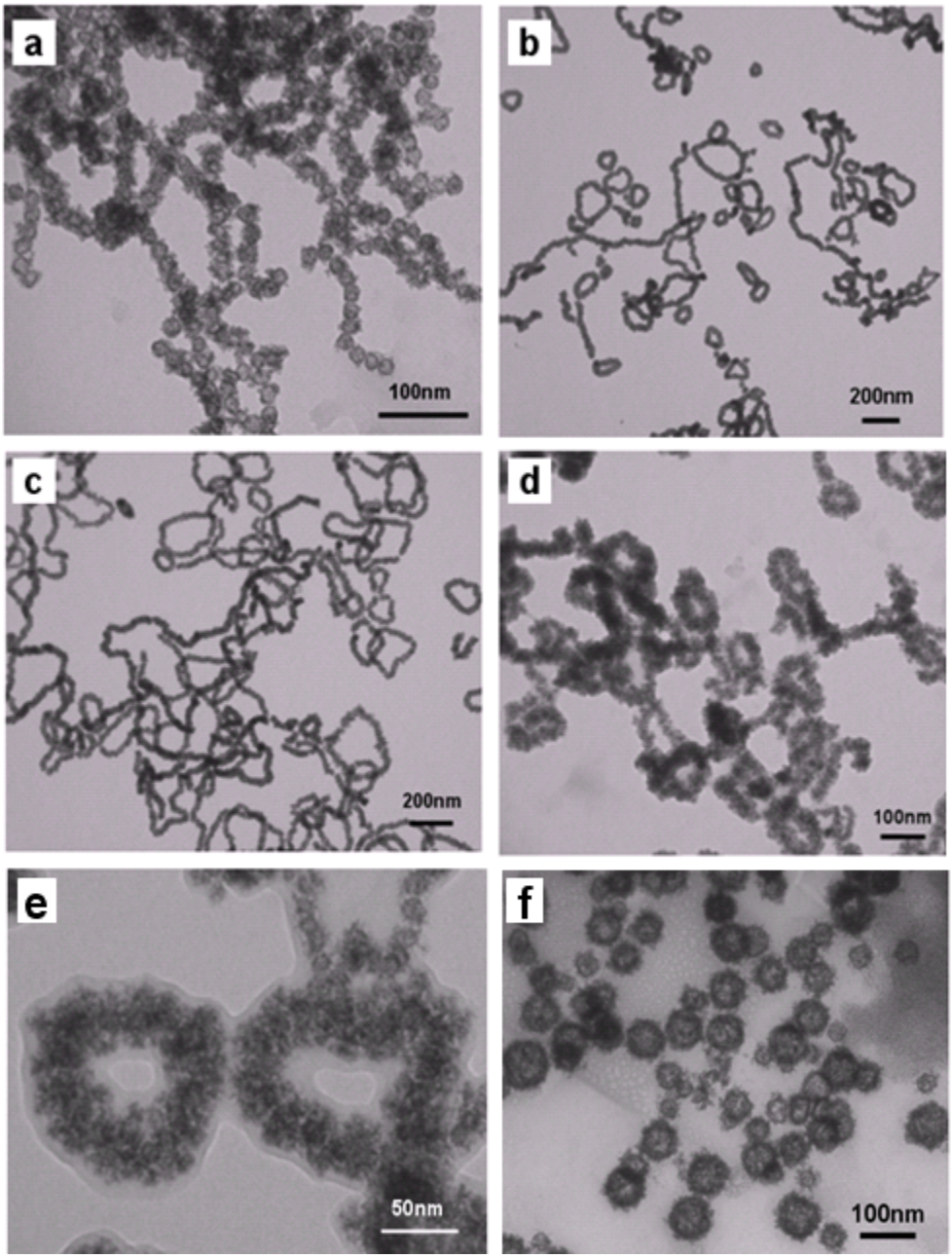


**Fig.S2** TEM images of CoPt hollow nanoparticles obtained at a) 25°C, b) 40°C, c) 50°C, d, e) 75°C and f) 35°C with high concentration of sodium citrate.

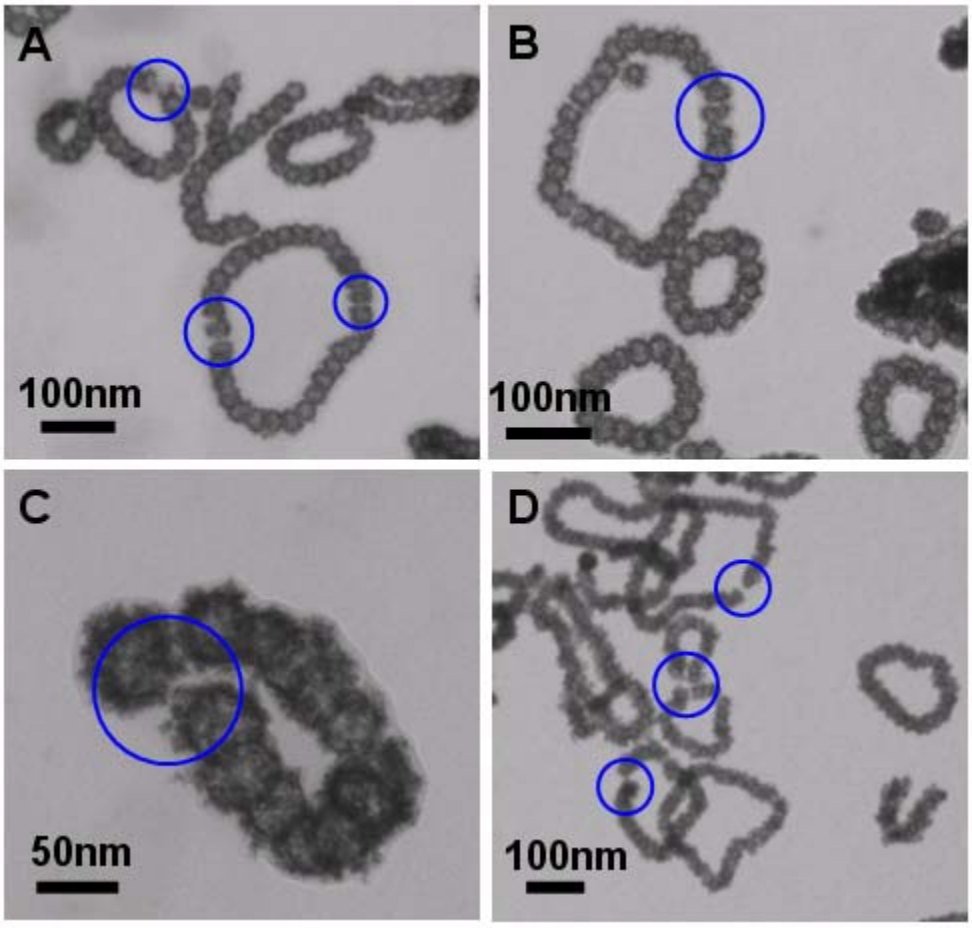


**Fig.S3** TEM images of ring-like CoPt hollow nanoparticles with non-spherical hollow particles and small interspace.

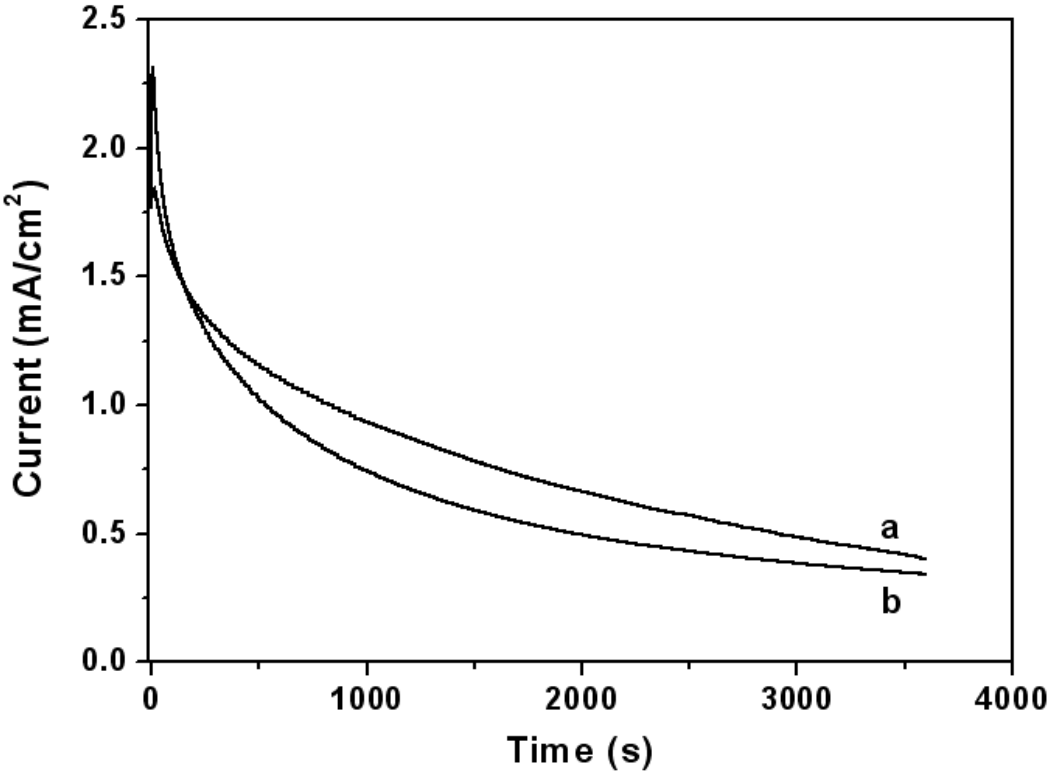


**Fig.S4** Chronoamperometry collected at 0.6 V (vs Ag/AgCl) in 0.5 M $H_2SO_4$ and 1 M methanol for a) chain-like CoPt hollow nanoparticles and b) ring-like CoPt hollow nanoparticles (using a charge for hydrogen adsorption/desorption of 210 $\mu$C cm$^{-2}$ and assuming that Co has no effect on hydrogen adsorption/desorption behavior).

**Reference:**

1. Y. Vasquez, A. K. Sra and R. E. Schaak, *J. Am. Chem. Soc.,* 2005, **127**, 12504.

2. M. H. Huang, Y. D. Jin, H. Q. Jiang, X. P. Sun, H. J. Chen, B. F. Liu, E. K. Wang and S. J. Dong, *J. Phys. Chem. B.*, 2005, **109**, 15264.