Electronic Supplementary Information

Highly-branched mesoporous Au-Pd-Pt trimetallic nanoflowers blooming on reduced graphene oxide as oxygen reduction electrocatalyst

Experimental Details

Chemicals: Potassium tetrachloroplatinate (K_2PtCl_4, >99.9%), sodium chloropalladite (Na_2PdCl_4, 98%), Pluronic F127 (Mw=12600), hexadecylpyridinium chloride monohydrate (HDPC, 98%), Pluronic P123 (Mw =5750) and Brij 58 (Mw=1124) were purchased from Aladdin Co. Gold chloride ($HAuCl_4$, 99%) and L-ascorbic acid (AA, AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Commercial Pt/C catalyst was ordered from Alfa Aesar Co. All the chemicals were used as received without further purification. The water used in all experiments was ultrapure (Millipore, 18.2 ΩM).

Synthesis of Au-Pd-Pt NFs/rGO: In a typical synthesis of highly-branched mesoporous Au-Pd-Pt NFs/rGO, Pluronic F127 (14 mg) and HDPC (1 mg) dissolved in 5 mL H_2O to form a homogeneous solution, then $HAuCl_4$ (20 mM, 0.1 mL), Na_2PdCl_4 (20 mM, 0.4 mL) and K_2PtCl_4 (20 mM, 0.4 mL) were successively added into the vial, followed by AA (100mM, 0.9 mL). The mixture solution was stirred for 1 h at room temperature. Then freshly prepared rGO (3 mg in 1 mL aqueous solution obtained by hydrazine reduction of graphene oxide synthesized by modified Hummers method[1,2]) was added and kept stirring for another 1 h. The resulting colloidal products were collected by centrifugation at 8000 rpm for 10 min and washed three times with water.

Characterization: The particle morphology and composition were investigated using a Hitachi H-8100 EM transmission electron microscope (TEM) with an accelerating voltage of 100 kV. HRTEM images and HAADF-STEM images were obtained with a

JEM-2010 operating at 200 kV equipped with an energy dispersive spectrometer (EDS). X-ray diffraction (XRD) patterns were collected on D8 ADVANCE (Bruker AXS, Germany) diffractometer equipped with Cu Kα radiation. The mole ratio of nanoparticles was determined by the inductively coupled plasma atomic emission spectrophotometry (ICP-AES), which obtained by a Thermo Scientific iCAP6300 (Thermo Fisher Scientific, US). X-ray photoelectron spectroscopy (XPS) measurement was performed on an ESCALAB-MKII spectrometer (VG Co., United Kingdom) with Al Kα X-ray radiation as the X-ray source for excitation. The nitrogen physisorption isotherms were measured on a Quantachrome Autosorb 3.01 instrument, and samples were degassed for 24 h at 50 °C under vacuum before the measurements. Thermogravimetric analysis (TGA) were performed from room temperature to 800 °C under N_2 atmosphere.

Electrochemical Measurements: A conventional three-electrode cell was used to perform the electrochemical measurements. Ag/AgCl (saturated KCl) electrode served as reference electrode, Pt wire served as counter electrode, and a working electrode. The working electrode was a glassy-carbon Rotating Ring Disk Electrode (RDE). To prepare the working electrode, the different catalysts were mixed with ethanol, water, and Nafion (5%) (v: v : v=1 : 1 : 0.075) and sonicated for 10 min. Then 10 μg of the catalyst was cast on a RDE and dried under ambient condition. The electrochemical active surface area (ECSA) measurement was determined by integrating the hydrogen adsorption charge on the CV at room temperature in 0.1 M N_2-saturated $HClO_4$ solution. The potential scan rate was 50 mV s^{-1} for the CV measurement. ORR measurements were conducted in a 0.1 M $HClO_4$ solution purged with oxygen during the measurement. The scan rate and rotation rate for ORR measurement were 10 mV s^{-1} and 1600 rpm, respectively. The accelerated durability tests were performed at room temperature in O_2-saturated 0.1 M $HClO_4$ solutions by applying the cyclic potential sweeps between 0.6 and 1.1 V versus RHE at a sweep rate of 50 mV s^{-1} for 6000 cycles.

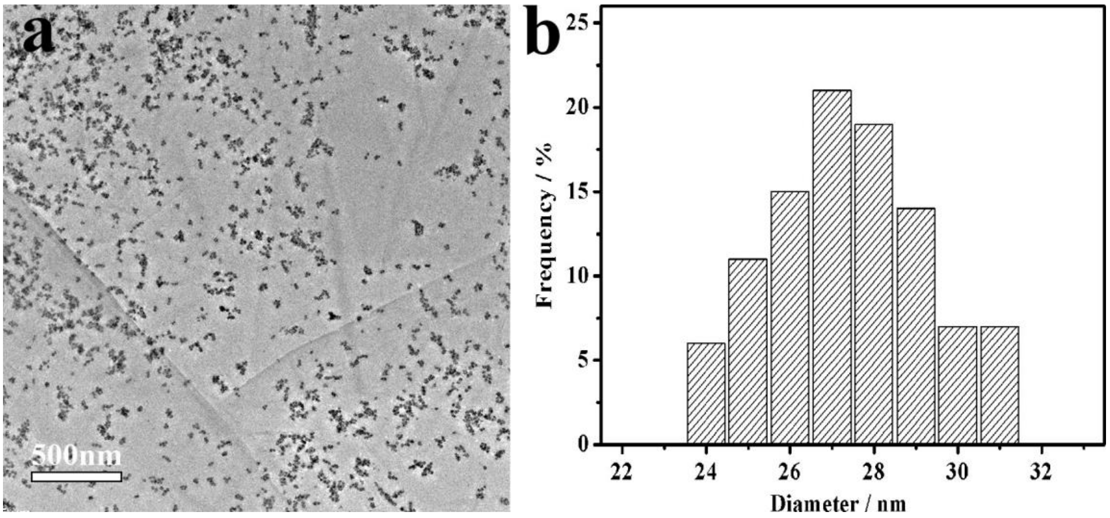

Fig. S1 (a) Additional TEM image and (b) the size distribution of the Au-Pd-Pt NFs/rGO.

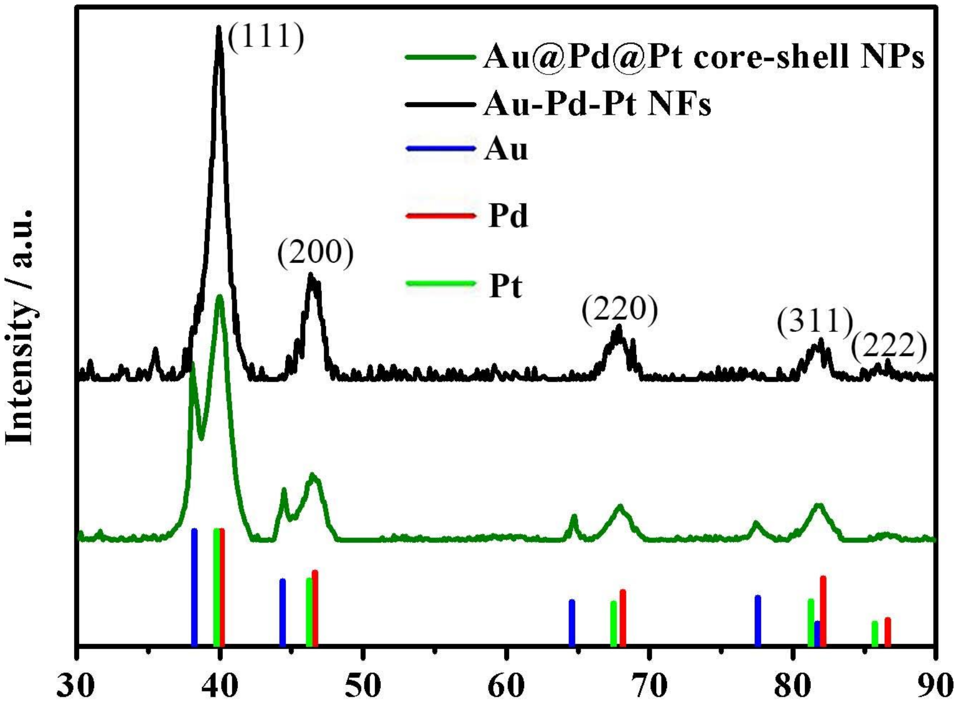

Fig. S2 Wide-angle XRD patterns of the typically prepared Au@Pd@Pt core-shell nanoparticles (corresponding to Fig. S5) and Au-Pd-Pt NFs.

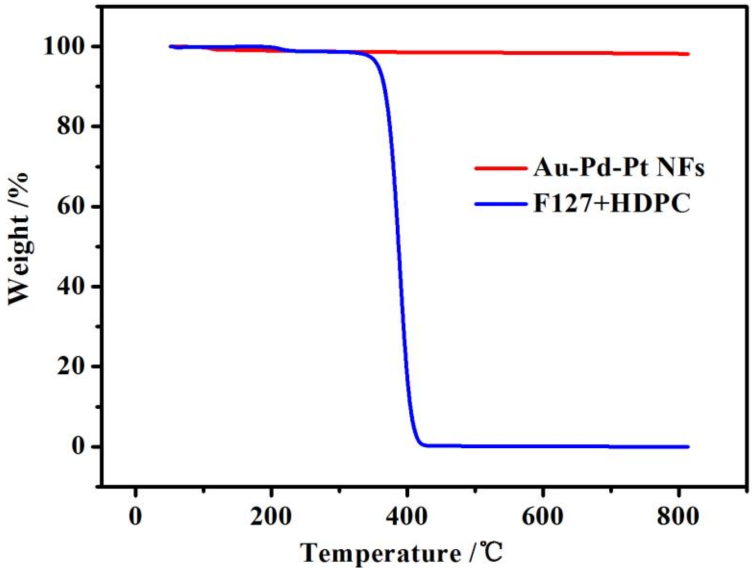

Fig. S3 TGA of the Au-Pd-Pt NFs and two surfactants compound performed from room temperature to 800 °C under N_2 atmosphere.

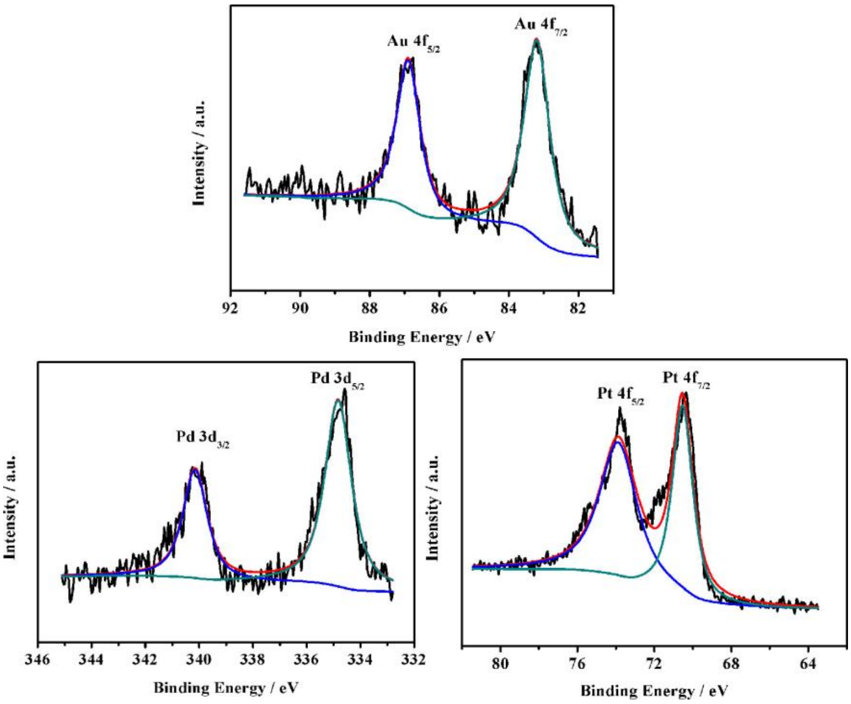

Fig. S4 XPS spectra for the Au 4f region (Au $4f_{7/2}$ and Au $4f_{5/2}$), Pd 3d region (Pd $3d_{5/2}$ and Pd $3d_{3/2}$) and Pt 4f region (Pt $4f_{7/2}$ and Pt $4f_{5/2}$) for the Au-Pd-Pt NFs.

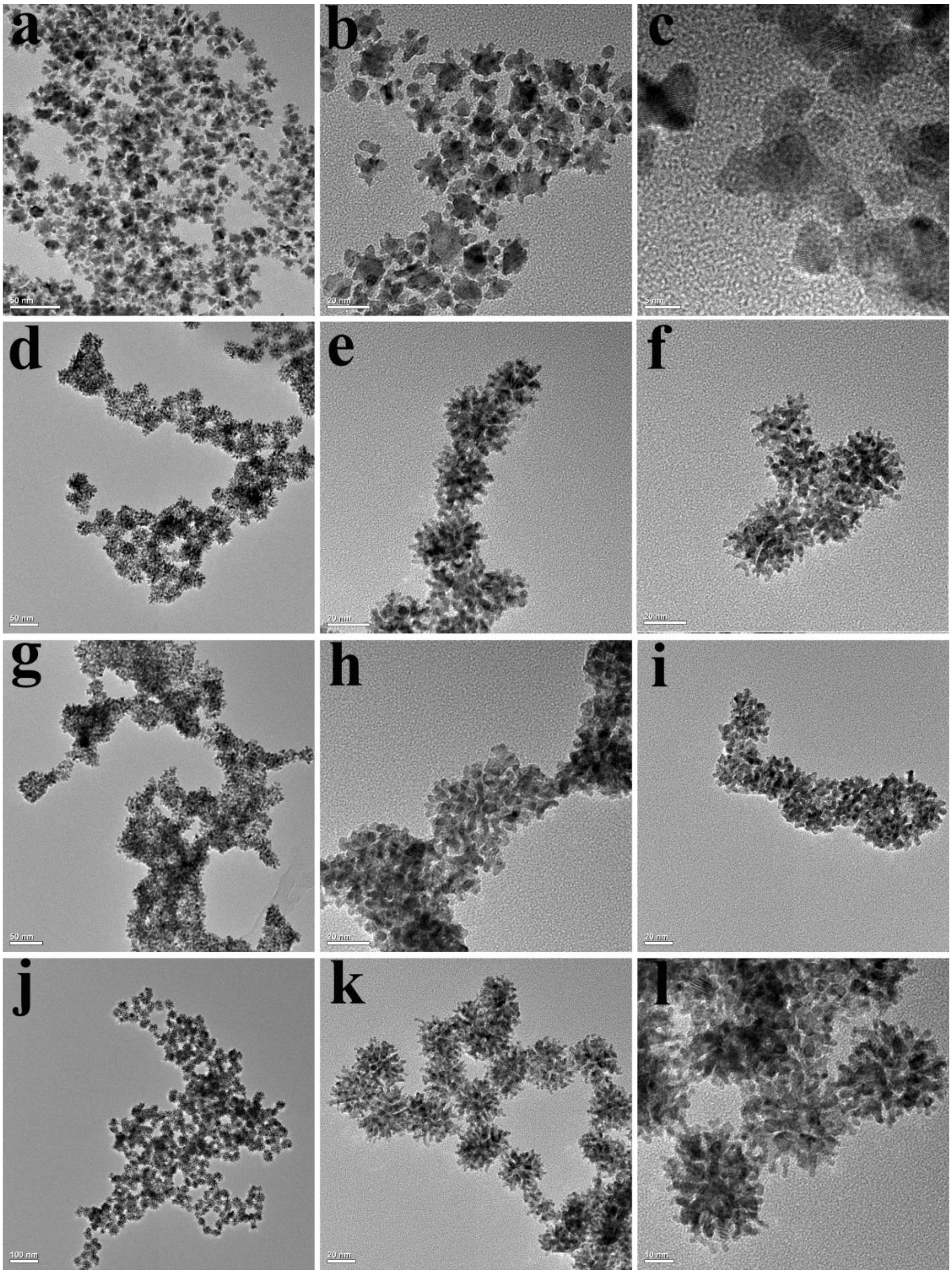

Fig. S5 TEM images of the trimetallic nanocrystals prepared under the same conditions but change the mole ratio of Au: Pd: Pt into (a, b, c) 1: 1: 1, (d, e, f) 1: 2: 4, (g, h, i) 1: 4: 2 and (j, k, l) 1: 4: 6.

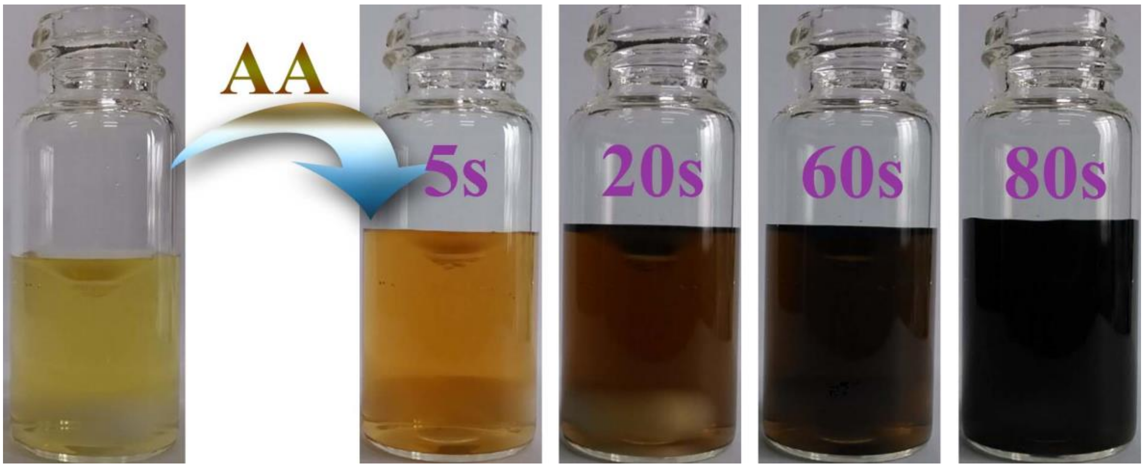

Fig. S6 Photographs of reaction solution reacted under different reaction times.

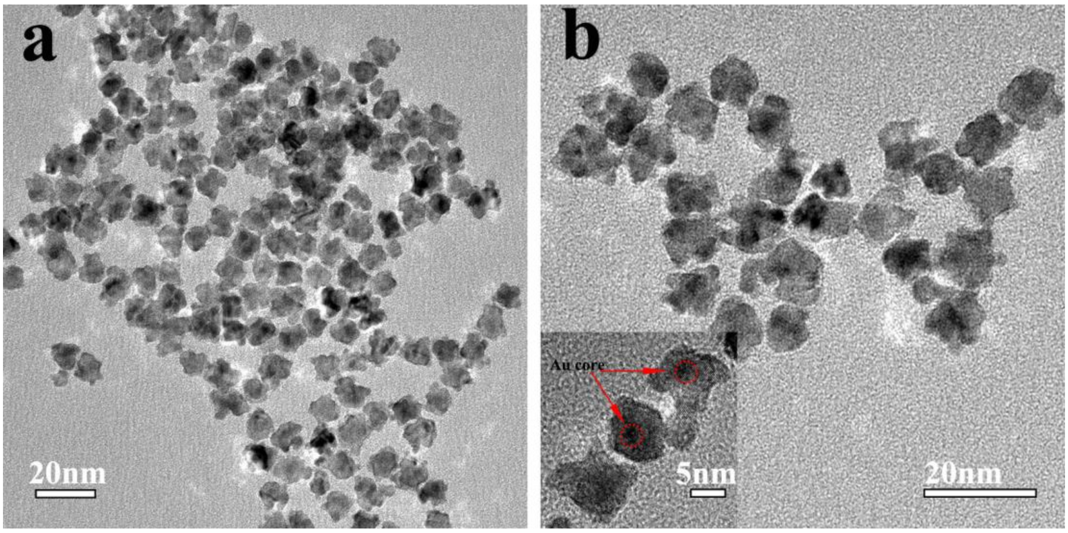

Fig. S7 TEM images of the products prepared under the same conditions as the synthesis of Au-Pd-Pt nanocrystals but in the absence of HDPC.

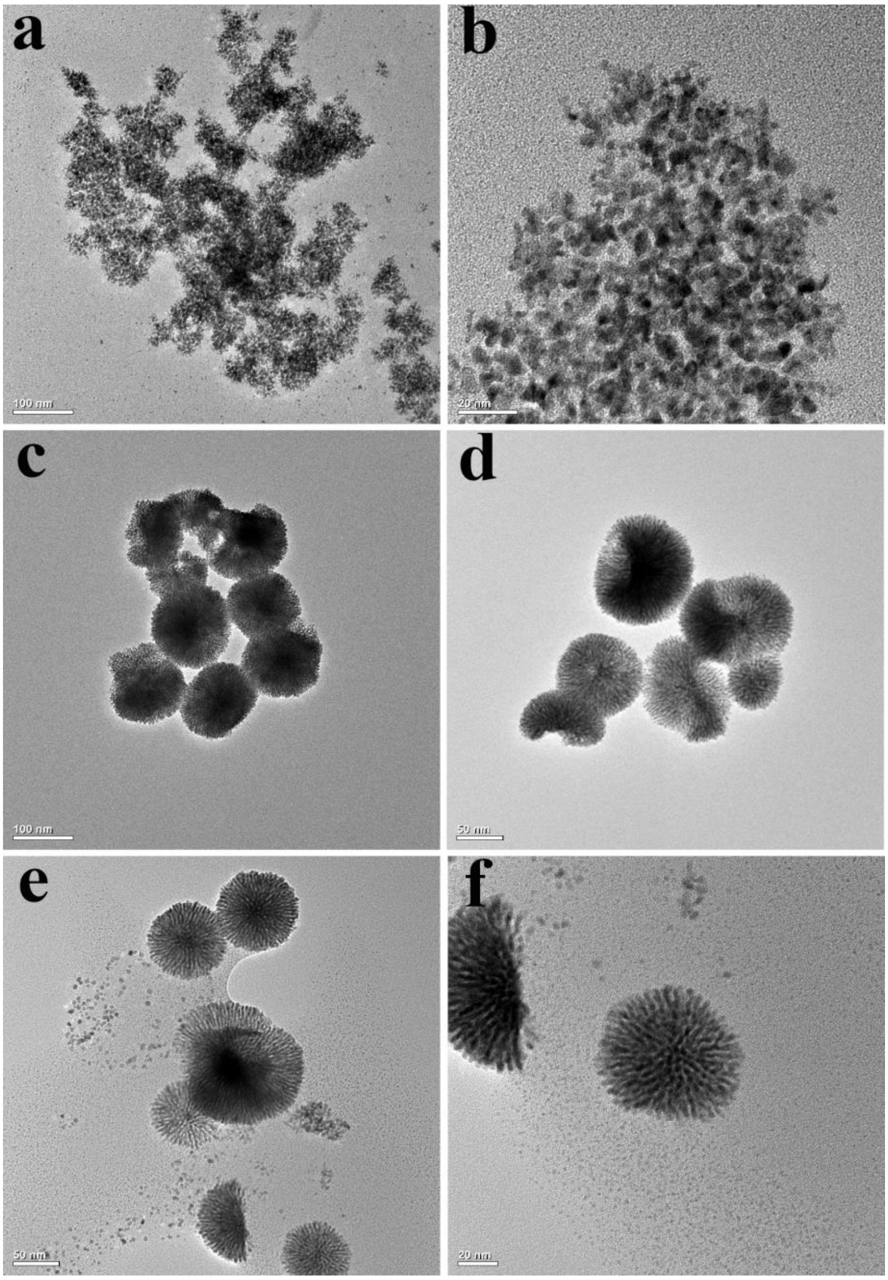

Fig. S8 TEM images of the products prepared under the same conditions as the synthesis of Au-Pd-Pt nanocrystals but with different amount of Pluronic F127 and HDPC: (a, b) 15 mg, 3mg, (c, d) 0 mg, 1mg and (e, f) 0 mg, 10 mg.

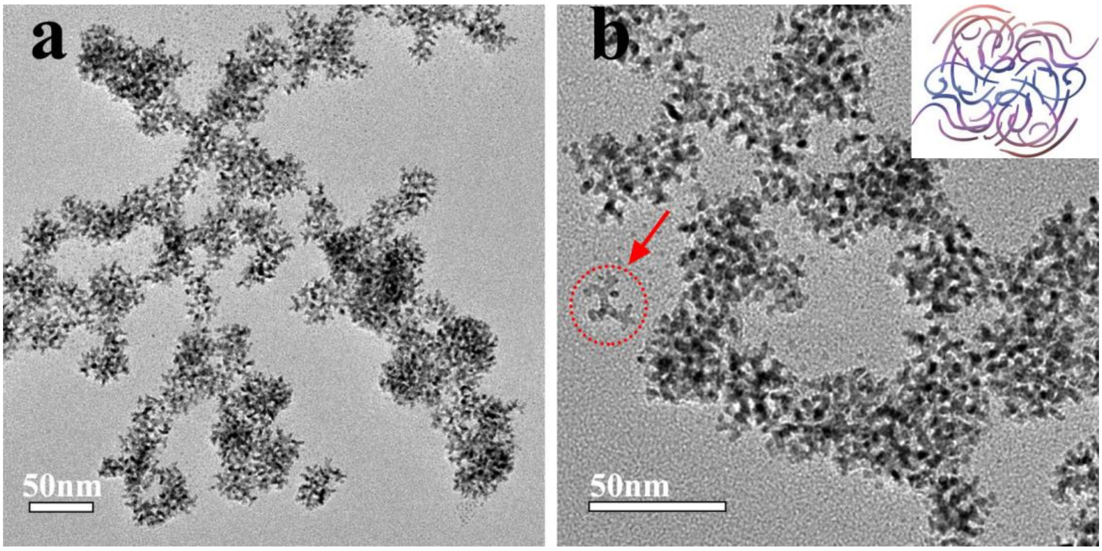

Fig. S9 TEM images of the products prepared under the same conditions as the synthesis of Au-Pd-Pt nanocrystals but in the absence of $HAuCl_4$.

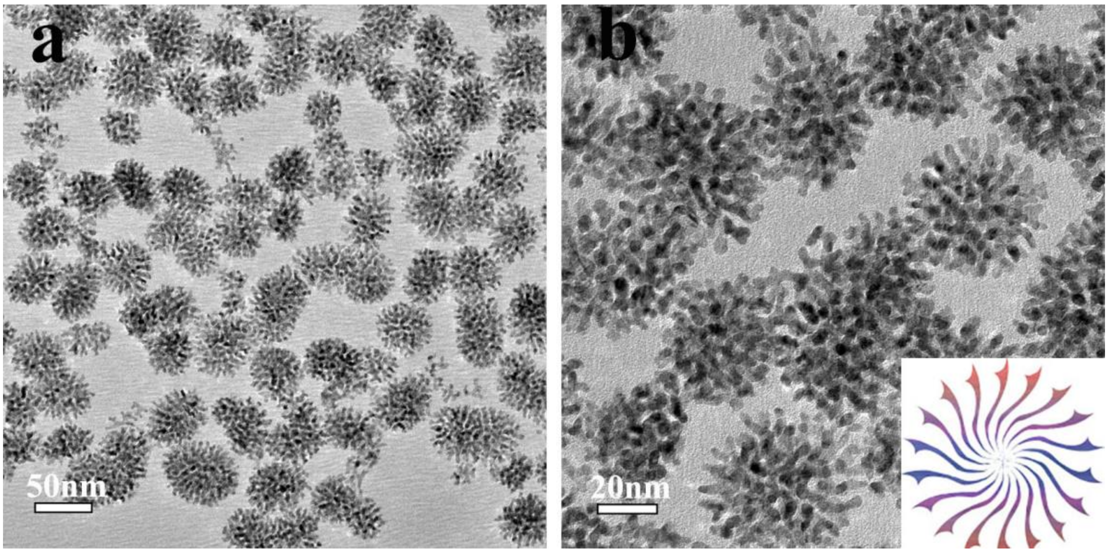

Fig. S10 TEM images of the products prepared under the same conditions as the synthesis of Au-Pd-Pt nanocrystals but replaced the Pluronic F127 with Pluronic P123.

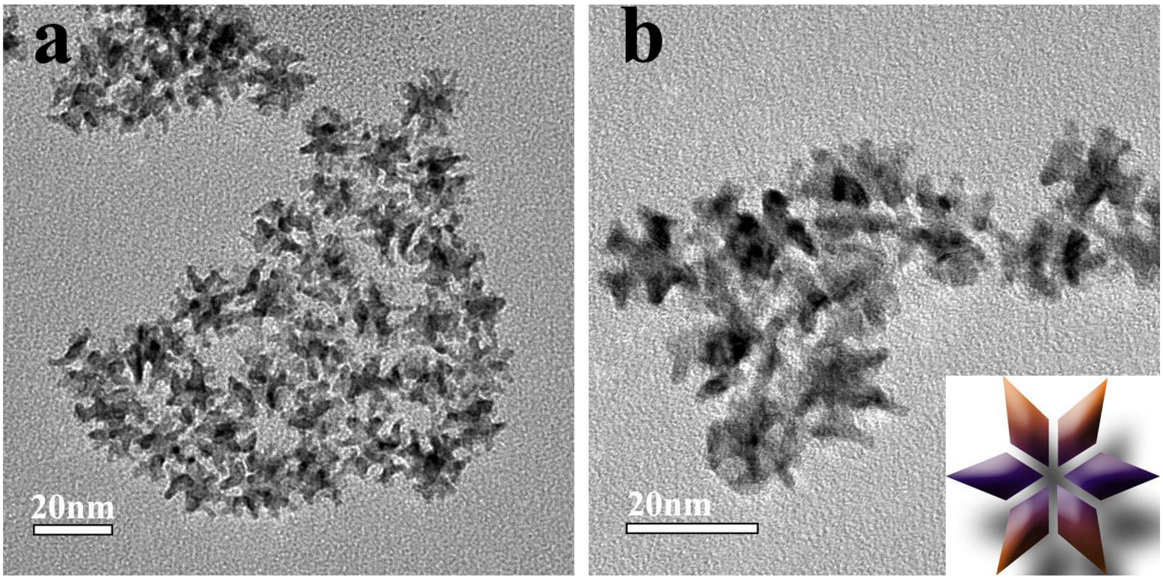

Fig. S11 TEM images of the products prepared under the same conditions as the synthesis of Au-Pd-Pt nanocrystals but replaced the Pluronic F127 with Brij 58.

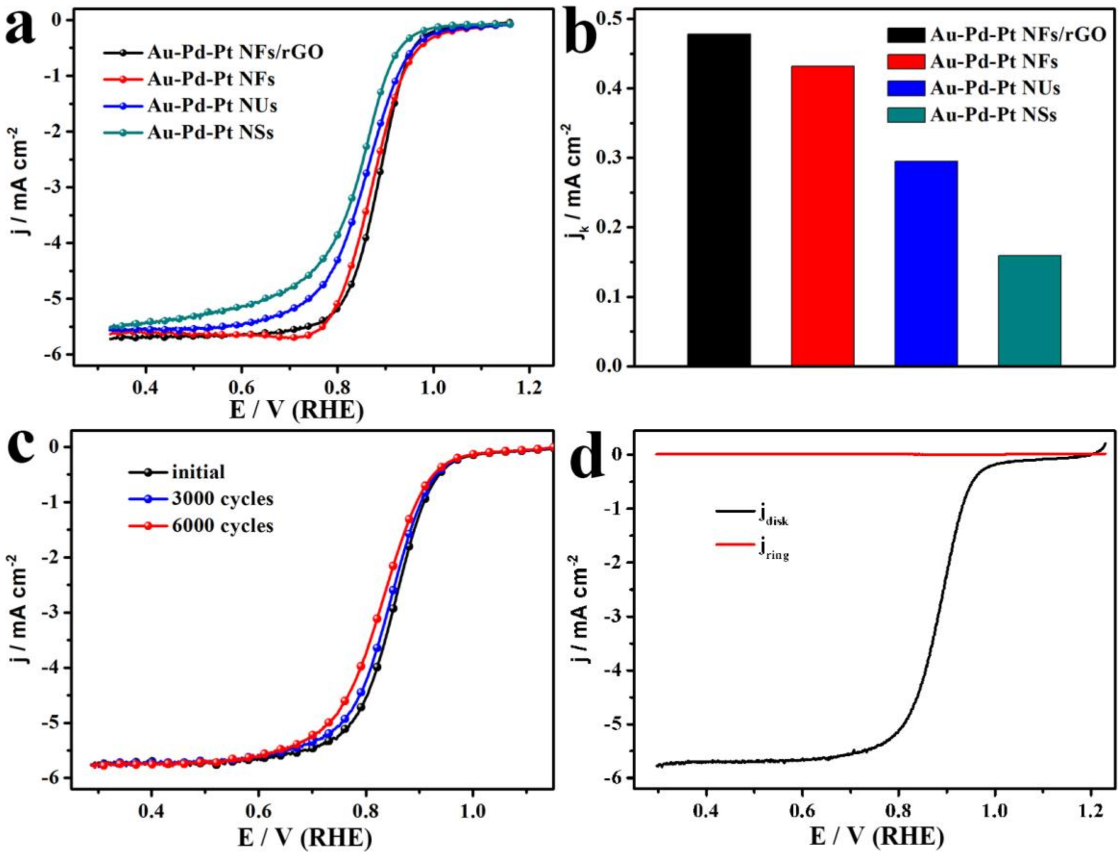

Fig. S12 (a) ORR polarization curves and (b) the histogram of the kinetic current for the Au-Pd-Pt NFs/rGO, Au-Pd-Pt NFs, Au-Pd-Pt NUs (corresponding to Fig. S10) and Au-Pd-Pt NSs (corresponding to Fig. S11). (c) ORR polarization curves for the Pt/C catalyst after prolonged cycles of CV. (d) RRDE voltammograms of the Au-Pd-Pt NFs/rGO in an O_2-saturated 0.1 M $HClO_4$ aqueous solution with a sweep rate of 10 mV s^{-1} and a rotation rate of 1600 rpm.

The electron transfer number calculate from rotating ring-disk eletrode (RRDE) measurement:

$$n = 4 \times \frac{I_d}{I_d + I_r / N}$$

Where I_d is disk current, I_r is ring current and N is current collection efficiency (N) of the Pt ring. N was determined to be 0.44 from the reduction of $K_3Fe[CN]_6$.

References

1. W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
2. S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, R. S. Ruoff, *Carbon*, 2007, **45**, 1558.