Electronic Supplementary Information

Bubble-assisted growth of hollow palladium nanospheres with structure control allowing very thin shells for highly enhanced catalysis

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Experimental section

Materials. Potassium chloropalladite (K_2PdCl_4) and Cetyl trimethylammonium bromide (CTAB) were provided by Shanghai Jingchun Reagent Co. Ltd. (Aladdin reagent). Formic acid (88 wt%), hydrazine hydrate (N_2H_4•H_2O, 85 wt%) and ethanol were purchased from Shanghai Chemical Reagent Co. Ltd. They are analytical grade and used as received without further purification. Deionized water with resistivity exceeding 18.0 mΩ•cm was from a JL-RO 100 Millipore-Q Plus water purifier.

Synthesis of hollow Pd nanospheres. In a typical synthesis, 7.5 mg K_2PdCl_4 was dissolved in a water-ethanol mixed solvent (6 mL of ethanol and 7 mL of deionized water) at room temperature (r.t.). The addition of 2 mL formic acid (88 wt%) obtains a colorless solution with C_{Pd} = 1.5 mM and C_{HCOOH} = 2.88 M. The mixture was transferred into a 25 mL Teflon-lined autoclave which was held at a constant temperature of typically 100 °C for 24 h. The product was collected by centrifugation (12000 rpm), washed, and dried in a vacuum oven at 40 °C.

Characterizations. The morphology and size of the products were characterized by scanning electron microscopy (SEM) on a field emission SEM microscope (Sirion XL, FEI, Hillsboro, OR) at 10 kV accelerating voltage. The structure of the products was analyzed by transmission electron microscopy (TEM), selected area electron diffraction (SAED), and high-resolution TEM (HRTEM) on an FEI TECNAI F20 microscope operating at an acceleration voltage of 200 kV. The composition and crystallographic properties were investigated by X-ray diffraction (XRD) on a Rigaku Ultima III diffractometer using Cu Kα = 1.5418 Å radiation. N_2 adsorption isotherms were measured at 77 K on a Micromeritics ASAP2020 instrument. Specific surface areas and pore-size distribution were determined using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively.

Electrochemical measurements. An evolution of electro-catalytic performance of the Pd shells was performed on a CHI-660D electrochemical workstation (Chenhua, Shanghai). A platinum foil was used as the counter electrode and a saturated calomel electrode (SCE) as the reference. The working electrode was a glassy carbon electrode (GCE) of 4 mm in diameter. Prior to surface coating, the GCE was sequentially polished with 1.0, 0.3, and 0.05 μm alumina slurry and then washed ultrasonically in water and ethanol for 5 minutes. 5.0 mg of dried Pd products and 100 μL Nafion ethanol solution (5 wt %) were dispersed ultra-sonically in 5 mL Millipore water. Then, 5 μL of suspension was drop-cast onto the GCE. Finally, the electrode was dried in an oven at 40 °C for 30 min. The mass loading on the electrode (in mg/cm^2) is the same for all the tests.

Supplementary figures and captions

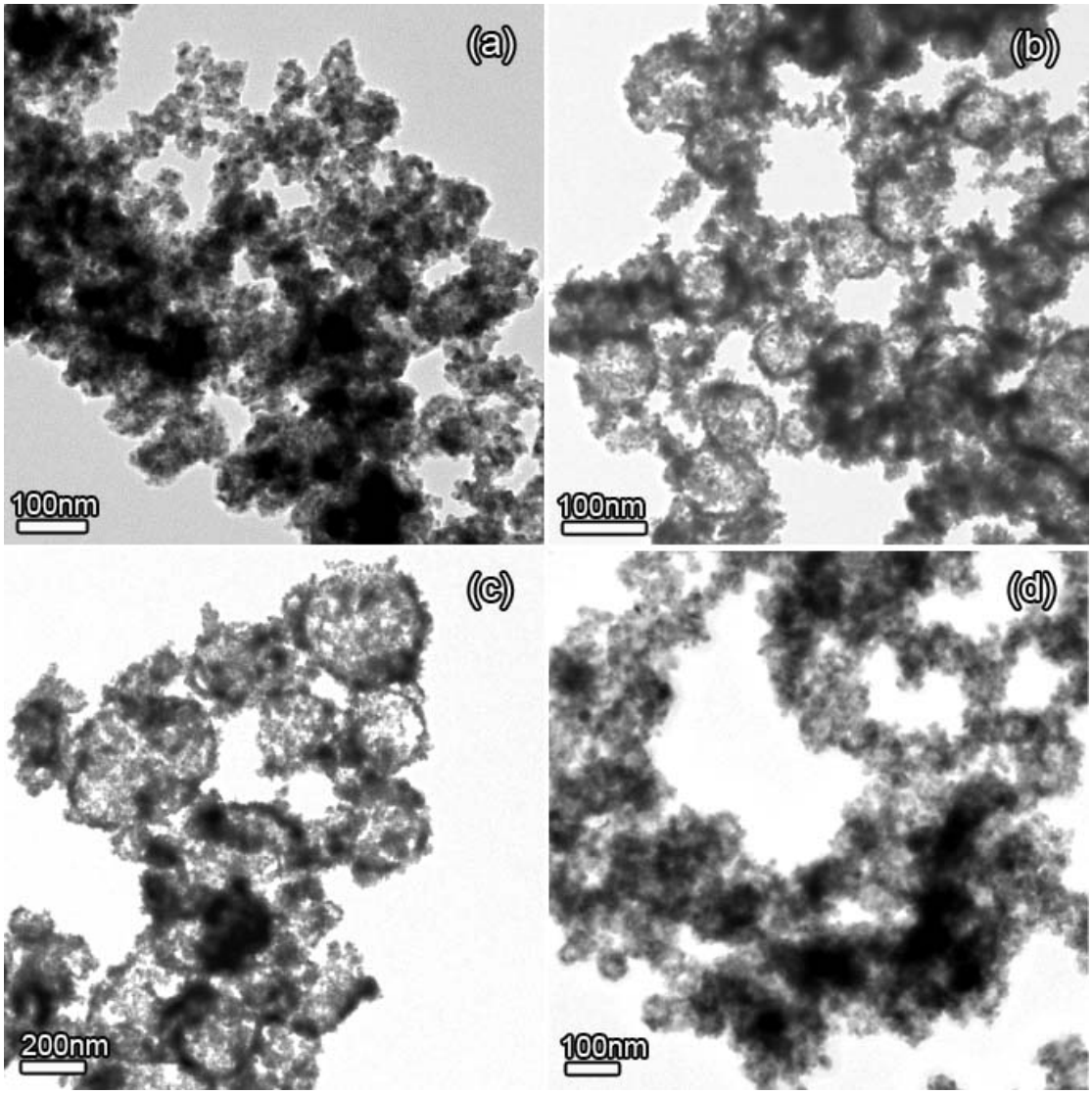

Figure S1. TEM image showing Pd products obtained with different C_{HCOOH} of 0.72 (a), 1.44 (b), 5.76 (c) and 6.0 (d) M when other reaction conditions are typical.

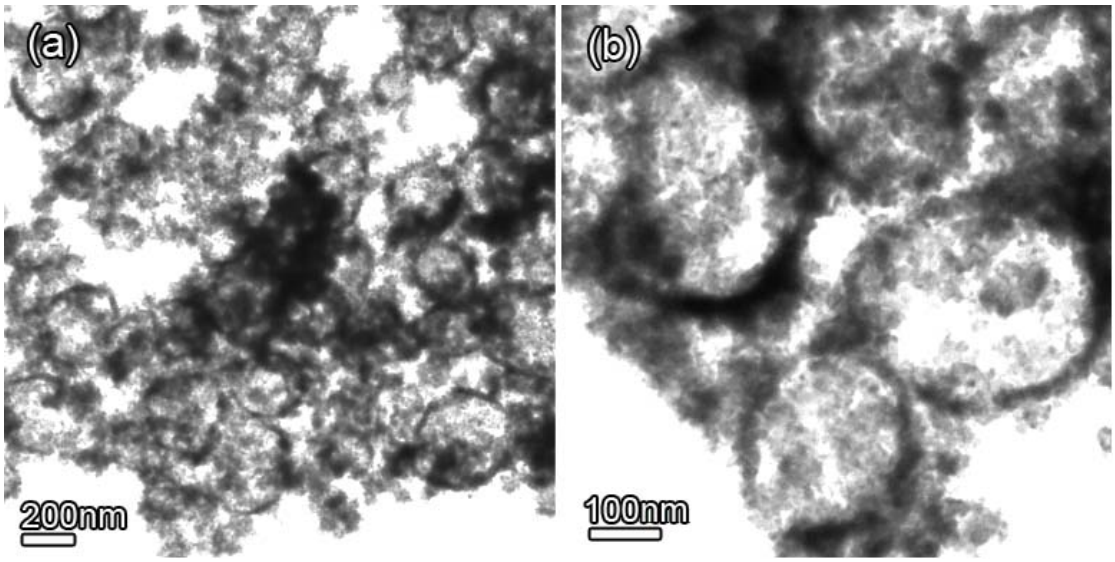

Figure S2. TEM images of hollow Pd spheres obtained with an addition of 0.2 mmol CTAB and C_{HCOOH} 5.04 M while other conditions are typical.

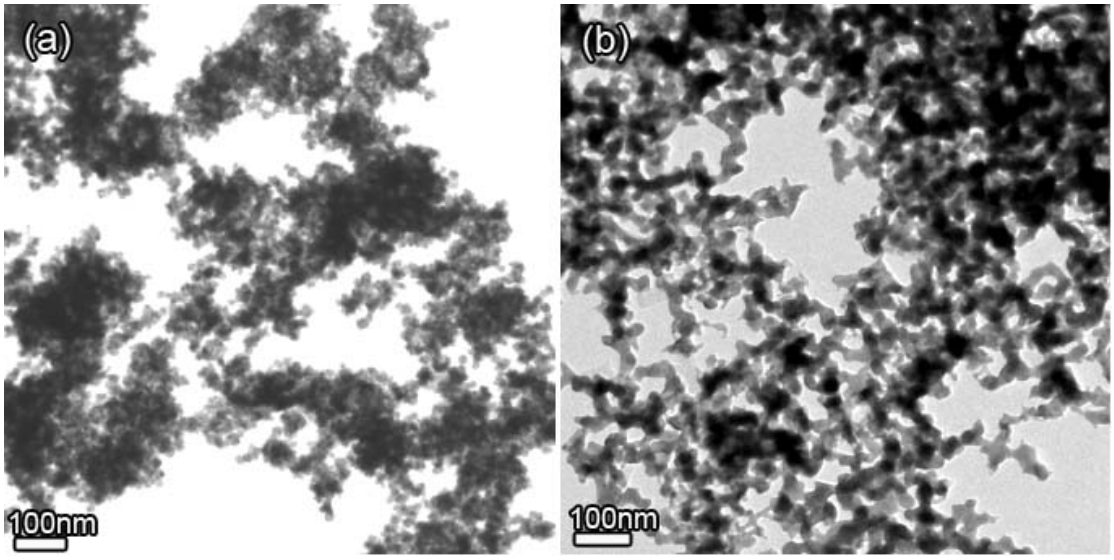

Figure S3. TEM images of Pd products obtained with different C_{Pd} of 0.8 mM (a) and 5.0 mM while keeping C_{HCOOH} at the typical 2.88 M.

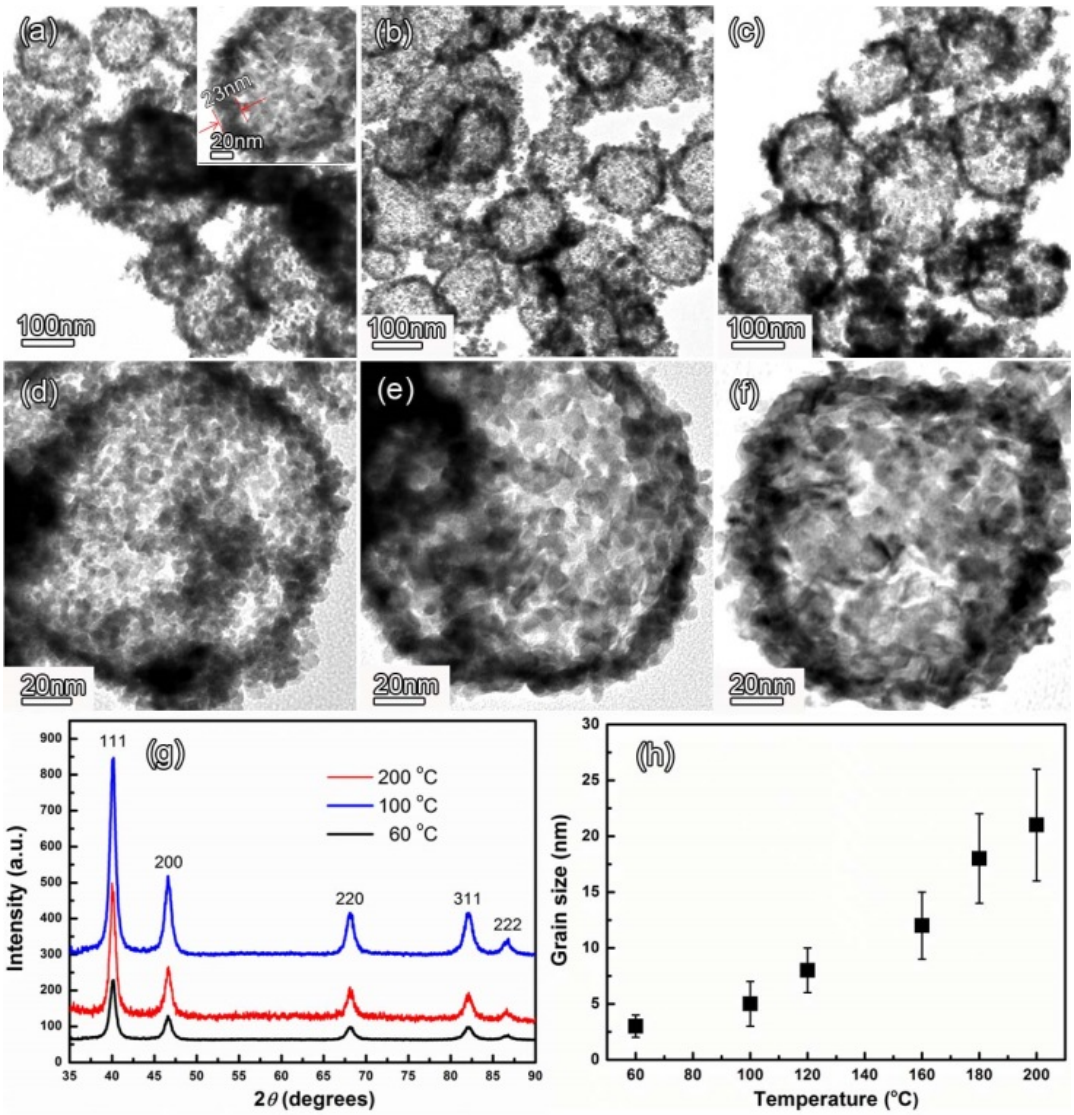

Figure S4. TEM images of the products with (C_{Pd}/mM, C_{HCOOH}/M) being (2.5, 2.88), (4.0, 2.88), and (4.0, 5.04) (a-c), isolated shells obtained with T = 60, 100, and 200°C (d-e), and corresponding XRD patterns (g) as well as the T-dependence of the grain size (h).

Table S1. Summary of reaction conditions and corresponding Pd shell parameters

C_{Pd} / mM	C_{HCOOH} / M	T / °C	d / nm	h / nm	Grain size / nm	Figure
1.5	1.44	100	85 ± 13	13 ± 4	5 ± 2	/
1.5	2.16	100	122 ± 22	21 ± 4	5 ± 2	2a
1.5	2.88	100	145 ± 25	16 ± 4	5 ± 2	1c
1.5	3.60	100	175 ± 28	12 ± 4	5 ± 2	2b
1.5	4.32	100	250 ± 30	10 ± 3	5 ± 2	2c
1.5	5.04	100	360 ± 35	7 ± 2	5 ± 2	2d
2.5	2.88	100	/	23 ± 4	/	3a
4.0	2.88	100	/	28 ± 5	/	3b
4.0	5.04	100	360 ± 35	18 ± 4	/	3c
1.5	2.88	60	/	/	4 ± 2	3d
1.5	2.88	100	/	/	6 ± 2	3e
1.5	2.88	160	/	/	11 ± 4	/
1.5	2.88	180	/	/	/	/
1.5	2.88	200	/	/	21 ± 7	3f

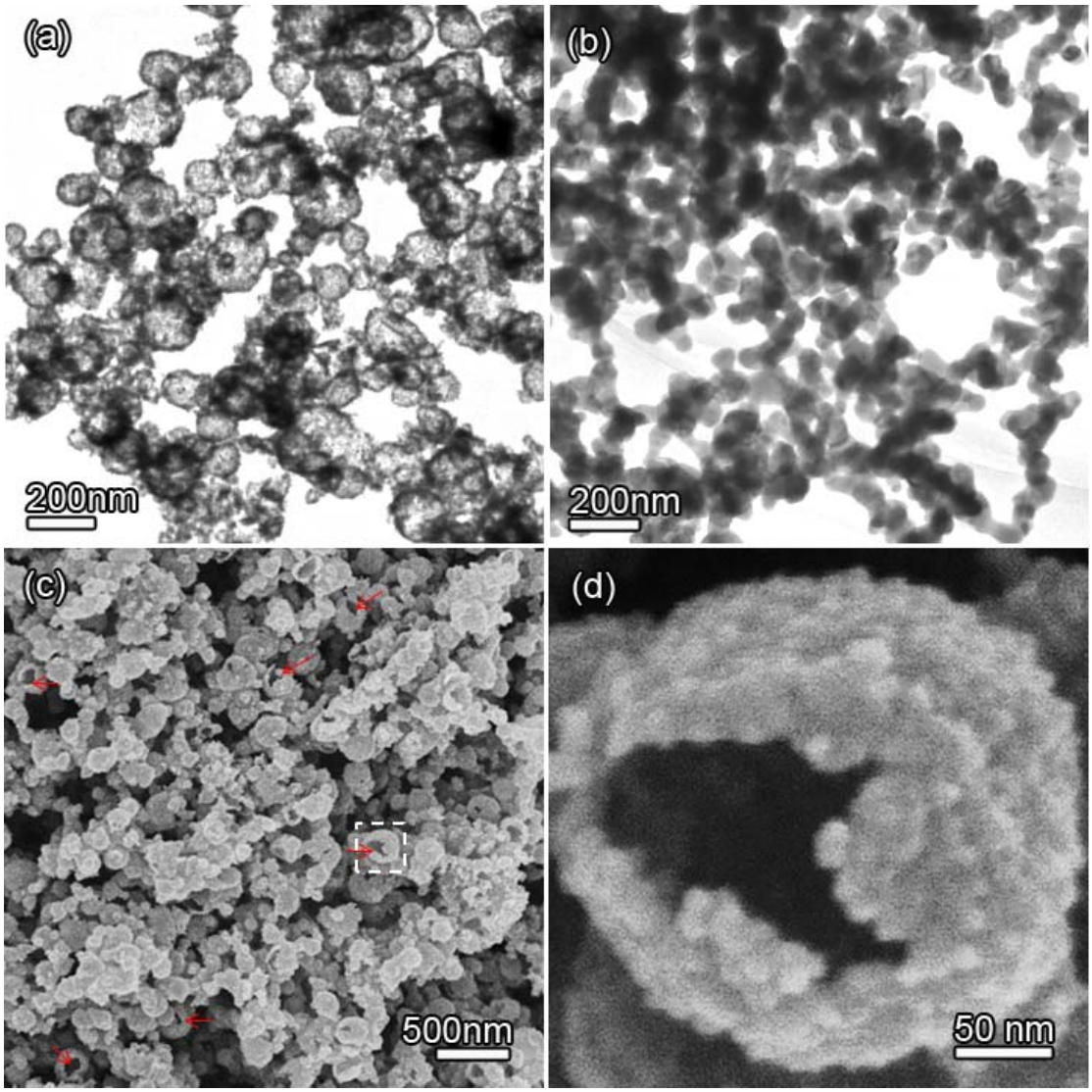

Figure S5. TEM images of Pd products obtained with autoclave filling ratios *r* of 65 % (a) and 75 % (b). SEM images (c-d) of the structures synthesized with *r* = 50 %.

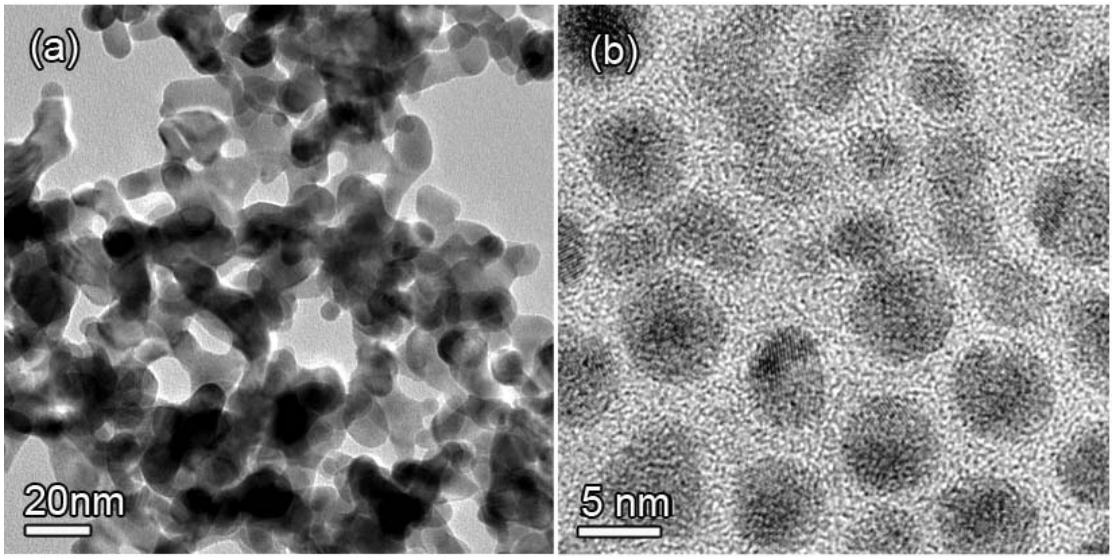

Figure S6. TEM images of commercial Sigma-Aldrich Pd black (a) and Pd NPs (b). These Pd nanostructures were used for electro-catalytic comparison.

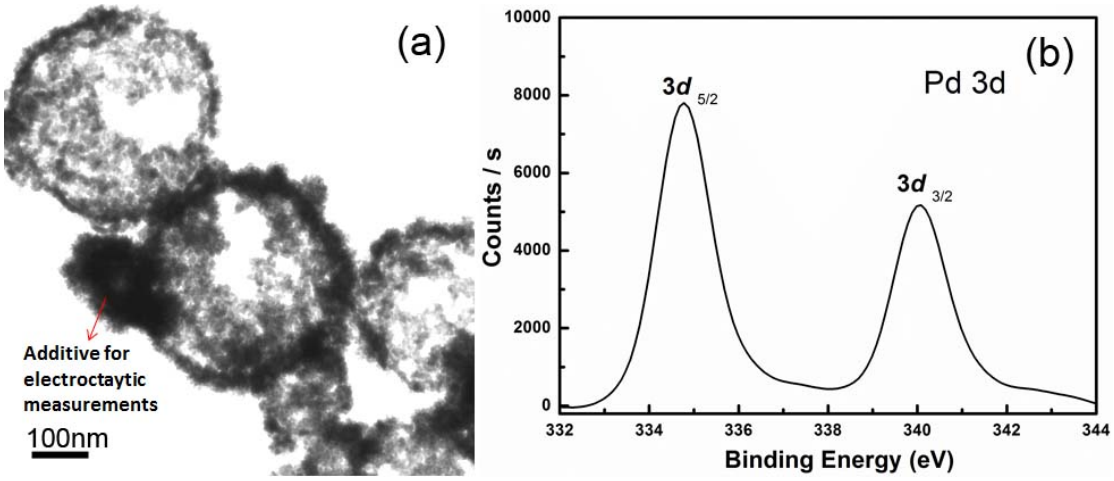

Figure S7. TEM image (a) and high resolution XPS spectrum (b) of the Pd-7 catalyst after the third successive electro-catalytic reaction cycle.