Supporting Information

Treelike Two-level Pd_xAg_y Nanocrystals Tailored for Bifunctional Fuel Cell Electrocatalysis†

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Experimental

Reagents and Chemicals

Palladium acetate ($Pd(O_2CCH_3)_2$) was obtained from Shanghai Jiuyue Chemical Co. Ltd. Silver nitrate ($AgNO_3$) was purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). 1-Naphthol ($C_{10}H_7OH$) was bought from Aladdin. Commercial Pd black was acquired from Johnson Matthey Corporation. All regents were used as received without further purification.

Characterizations

The morphology and structure of Pd_xAg_y NTs were characterized through Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), which were performed on a JEOL JEM-2100F transmission electron microscopy under an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) images and energy-dispersive X-ray (EDX) spectra were acquired on a Hitachi S5500 SEM. X-ray diffraction (XRD) patterns were acquired on a Model D/max-rC X-ray diffractometer using Cu Kα radiation source (λ = 1.5406 Å) and operating at 40 kV and 100 mA. X-ray photoelectron spectroscopy (XPS) measurements were proceeded on a Thermo VG Scientific ESCALAB 250 spectrometer with a monochromatic Al Kα X-ray source. The binding energy was calibrated by means of the C1s peak energy of 284.6 eV. Fourier transform infrared (FT-IR) was carried out using a Nicolet 520 SXFTIR spectrometer. The chemical composition of Pt_xAg_y NTs was investigated by EDX technique and inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Fig. S1 (a and b) Digital photos of the large-scale synthesis of Pd_3Ag_1 NTs, and (c) TEM image of the Pd_3Ag_1 NTs from large-scale synthesis.

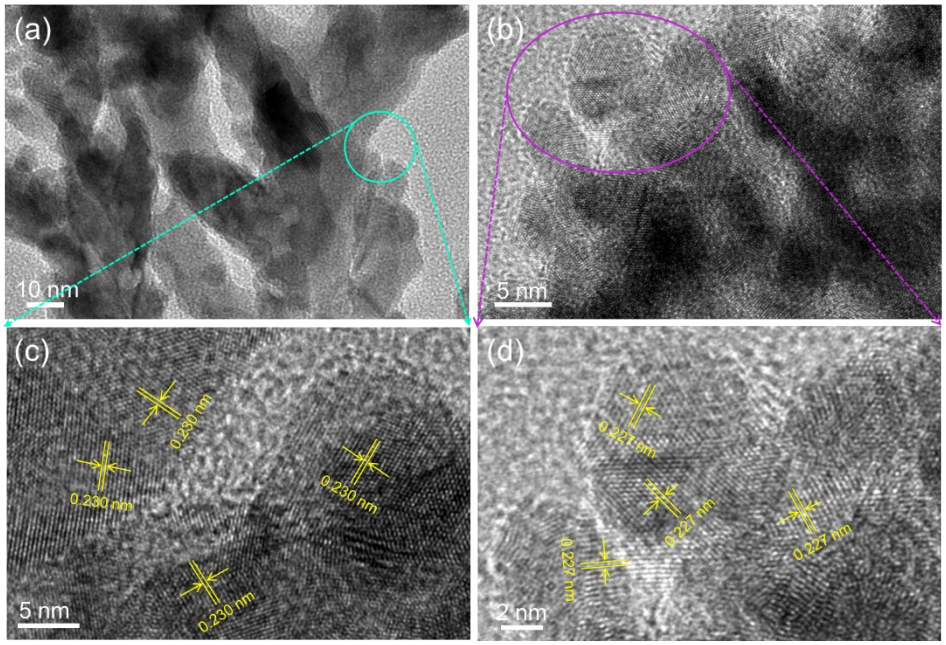

Fig. S2 TEM images and HRTEM images of the branches (a and c) and dendrites (b and d) in a Pd_3Ag_1 NT.

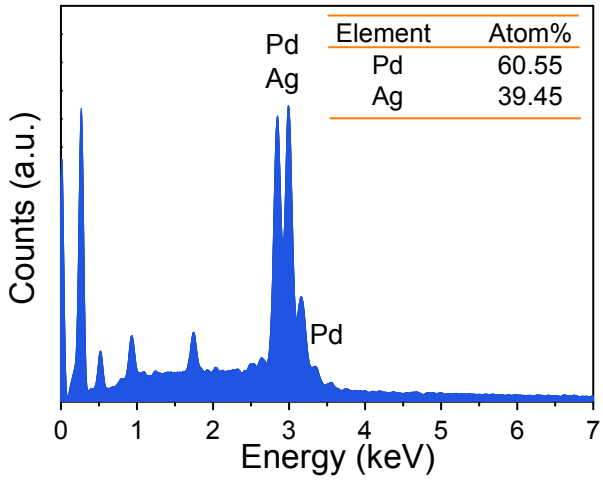

Fig. S3 EDX spectrum of Pd_3Ag_1 NTs.

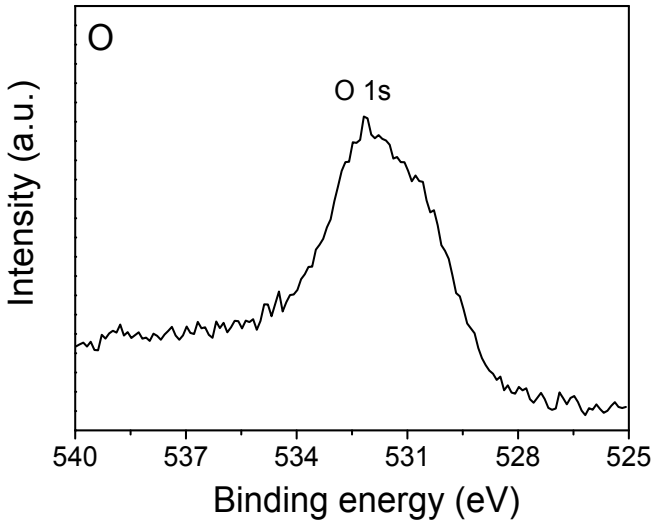

Fig. S4 XPS spectrum of Pd_3Ag_1 NTs in O 1s region.

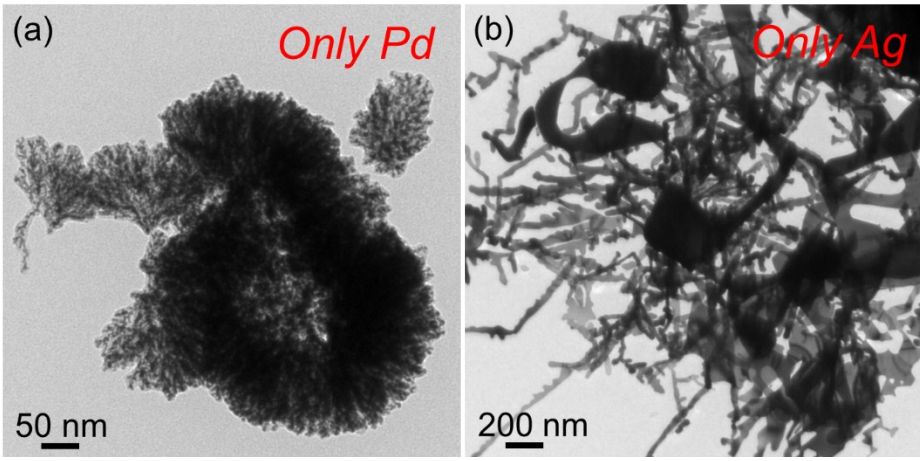

Fig. S5 TEM images of 3D dandelion-like tiny Pd nanodendrites (Pd NDs) and 2D Ag nanobelts (Ag NBs).

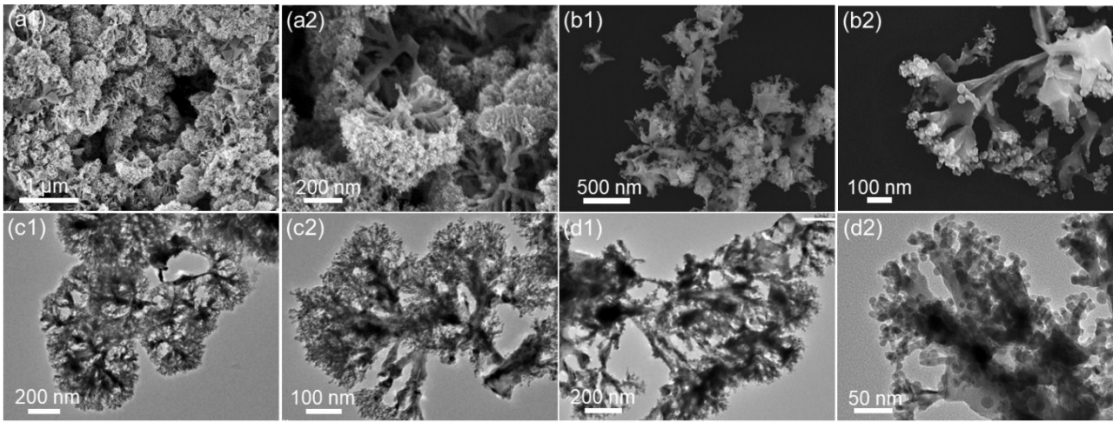

Fig. S6 SEM images of (a) Pd_1Ag_1 NTs and (b) Pd_1Ag_3 NTs, TEM images of (c) Pd_1Ag_1 NTs and (d) Pd_1Ag_3 NTs.

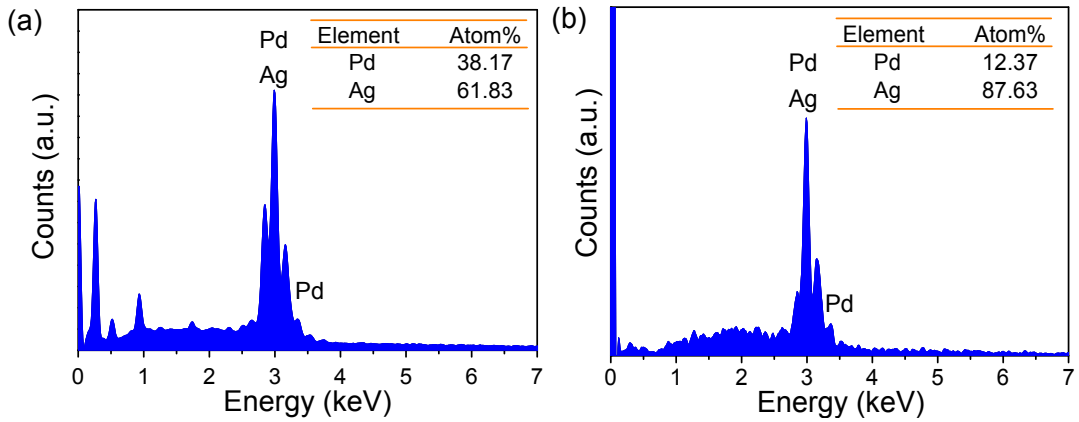

Fig. S7 EDX spectra of Pd_1Ag_1 NTs and Pd_1Ag_3 NTs.

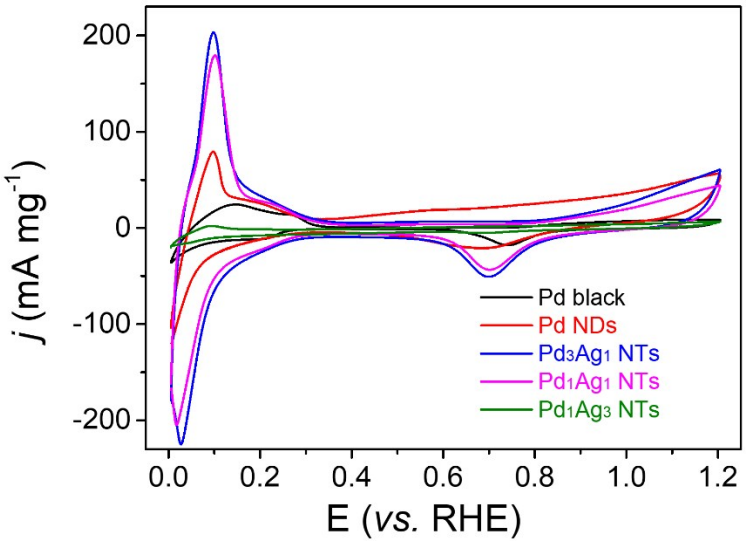

Fig. S8 Mass-normalized CV curves of the catalysts in N_2-saturated 0.5 M H_2SO_4 solution under a sweep rate of 50 mV s^{-1}.

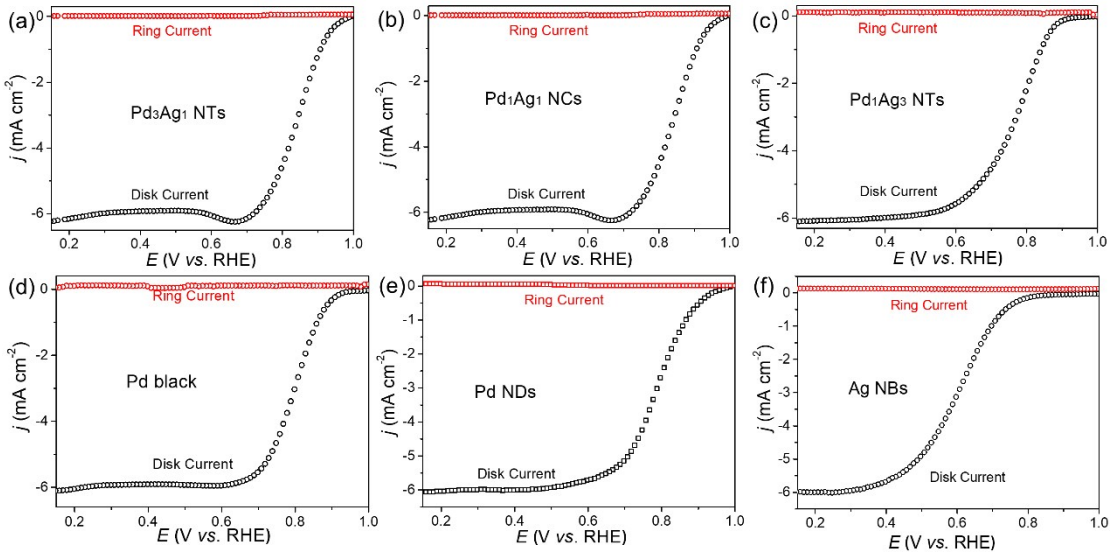

Fig. S9 RRDE curves for the ORR of catalysts: (a)Pd_3Ag_1 NTs, (b) Pd_1Ag_1 NTs, (c) Pd_1Ag_3 NTs, (d) Pd black, (e) Pd NDs and (f) Ag NBs.

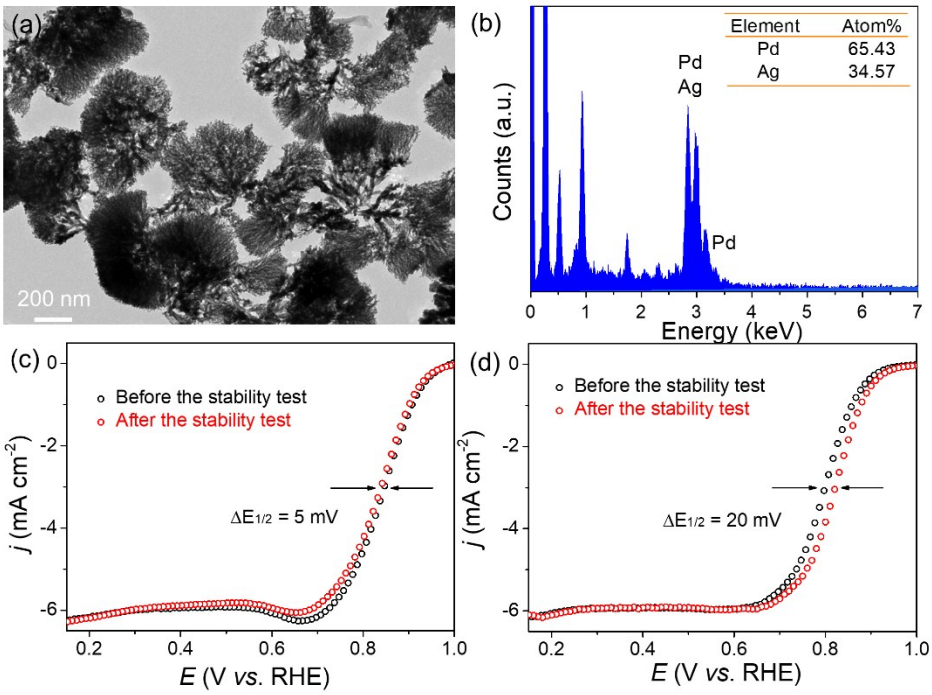

Fig. S10 (a) TEM image and (b) EDX spectrum of Pd_3Ag_1 NTs acquired after the chronoamperometric measurements in O_2-saturated 0.1 M KOH, ORR performance of (c) Pd_3Ag_1 NTs, (d) commercial Pd black before and after the stability test.

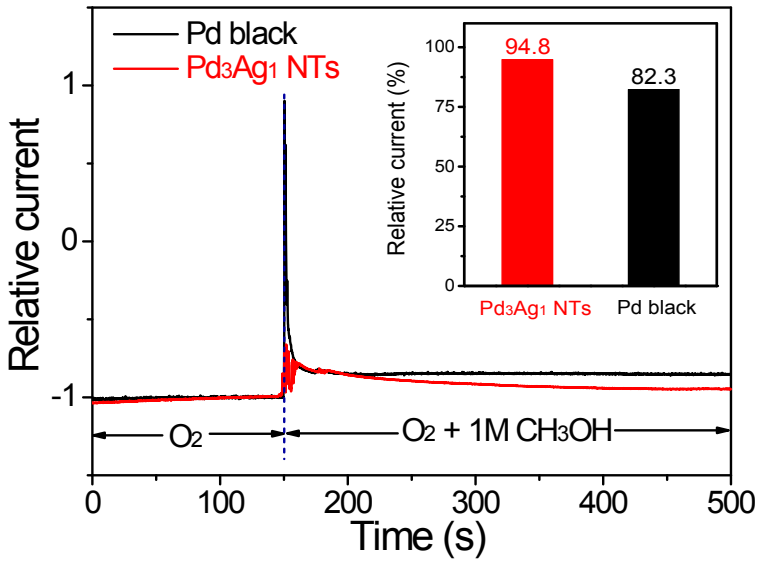

Fig. S11 Comparison of methanol resistance by chronoamperometric measurements at 0.5 V in O_2-saturated 0.1 M KOH (percentage of current retained *vs.* operation time).

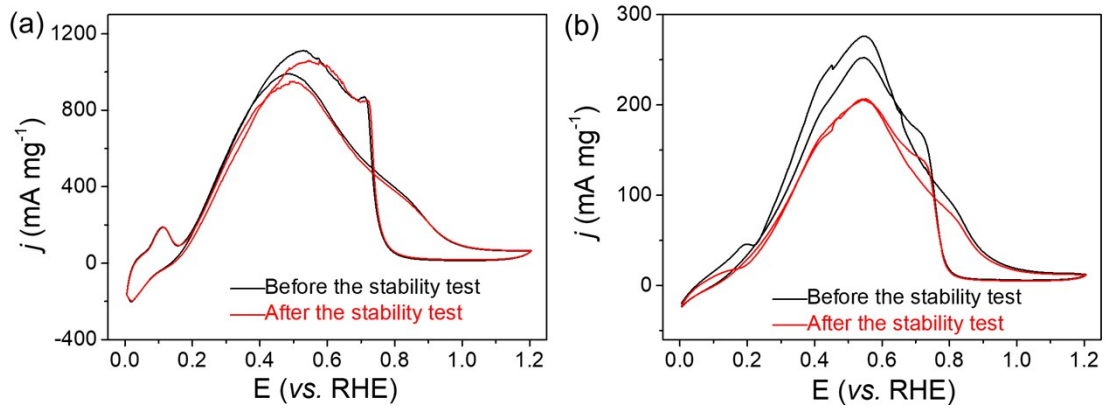

Fig. S12 FAOR performance of (c) Pd_3Ag_1 NTs, (d) commercial Pd black before and after the stability test.