Supporting Information

Surface engineering of ultrasmall supported Pd_XBi nanoalloys with enhanced electrocatalytic activity for selective alcohol oxidation

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Experimental

Materials and chemicals

Carbon black (Vulcan XC-72R) was purchased from Cabot Corp (USA). $Pd(NO_3)_2$ solution (0.94M $Pd(NO_3)_2$ and 0.19M HNO_3 , ≥ 99.9%) was obtained from Shanghai July Chemical Co. (P. R. China). Hydrazine hydrate (HHA, ≥ 85%, AR), ethylene glycol (EG, ≥99.0%, AR) Bismuth(Ⅲ) nitrate pentahydrate (AR, ≥ 99.0%), methanol (AR, ≥ 99.5%), ethanol (AR, ≥ 99.7%), 1-Propanol (AR, ≥ 99.5%), isopropanol (AR, ≥ 99.7%) were obtained from Sinopharm Chemical Reagent Co. (P. R. China). All the chemicals employed were used as received.

Synthesis of Pd_XBi/CB

CB (100 mg) was ultrasonically dispersed in EG (200 mL containing 1.60 mL HHA) to form a uniform suspension. After ultrasonication, 250 μL $Pd(NO_3)_2$ and $Bi(NO_3)_3$ mixed solution (containing 2.0 M HNO_3)* was added to the above reaction system, which was further stirred for about 15 min. The resulting product was centrifuged, washed, and finally dried at room temperature in a vacuum oven overnight.

Synthesis of Pd/CB

CB (100 mg) was ultrasonically dispersed in EG (200 mL containing 1.60 mL HHA) to form a uniform suspension. After ultrasonication, 250 μL $Pd(NO_3)_2$ with 0.2 M was added to the above reaction system, which was further stirred for about 15 min. The resulting product was centrifuged, washed, and finally dried at room temperature in a vacuum oven overnight.

Physical characterizations

Transmission electron microscopy (TEM) measurements were performed on a JEOL JEM-2100 microscope operating at 200 kV, by depositing a drop of sample dispersion onto 200 mesh Cu grids coated with a carbon layer. The powder XRD patterns were recorded on the Beijing Purkinjie general instrument XD-3 X-ray diffraction using Cu Kα radiation (λ ≈ 1.54 Å) at 35 kV and 20 mA (2θ from 10° to 80°). A glass slide was used to place the grinded sample. X-ray photo-electron spectroscopy (XPS) was performed on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Al K α radiation (hv = 1486.6 eV). Inductively coupled plasma-optical emission spectroscopy (ICP-OES) experiments was performed on a Varian 720-ES spectrometer.

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*For Pd_8Bi/CB synthesis, c[$Pd(NO_3)_2$] = 0.75 M, c[$Bi(NO_3)_3$] = 0.09 M;
For Pd_4Bi/CB synthesis, c[$Pd(NO_3)_2$] = 0.63 M, c[$Bi(NO_3)_3$] = 0.16 M;
For Pd_2Bi/CB synthesis, c[$Pd(NO_3)_2$] = 0.47 M, c[$Bi(NO_3)_3$] = 0.24 M.

Electrochemical measurements

Electro-catalytic activities of samples were measured in a conventional three-electrode cell using a CHI 760D electrochemical workstation. The electrode assembly consists of a Pt wire as the counter electrode, and a mercuric oxide electrode with double salt bridges as the reference electrode in alkaline medium, a glassy carbon disk (3 mm in diameter) coated with 10 μg catalyst as the working electrode. Before the preparation of the catalysts modified GCE, the GCE was polished with 1, 0.3 and 0.05 μm α-Al_2O_3, sequentially. 10 mg catalysts was ultrasonically dispersed in 5.0 mL mixture of water and 5% Nafion solution (v[water] : v[Nafion solution] = 60:1) for 1 min. 5 μL of as-prepared mixture was carefully injected on the gassy carbon disk and dried in the air for 3 h at room temperature. No ohmic-drop compensation was applied to any of the performed experiments. All the potentials were given on the reversible hydrogen electrode (RHE) scale.

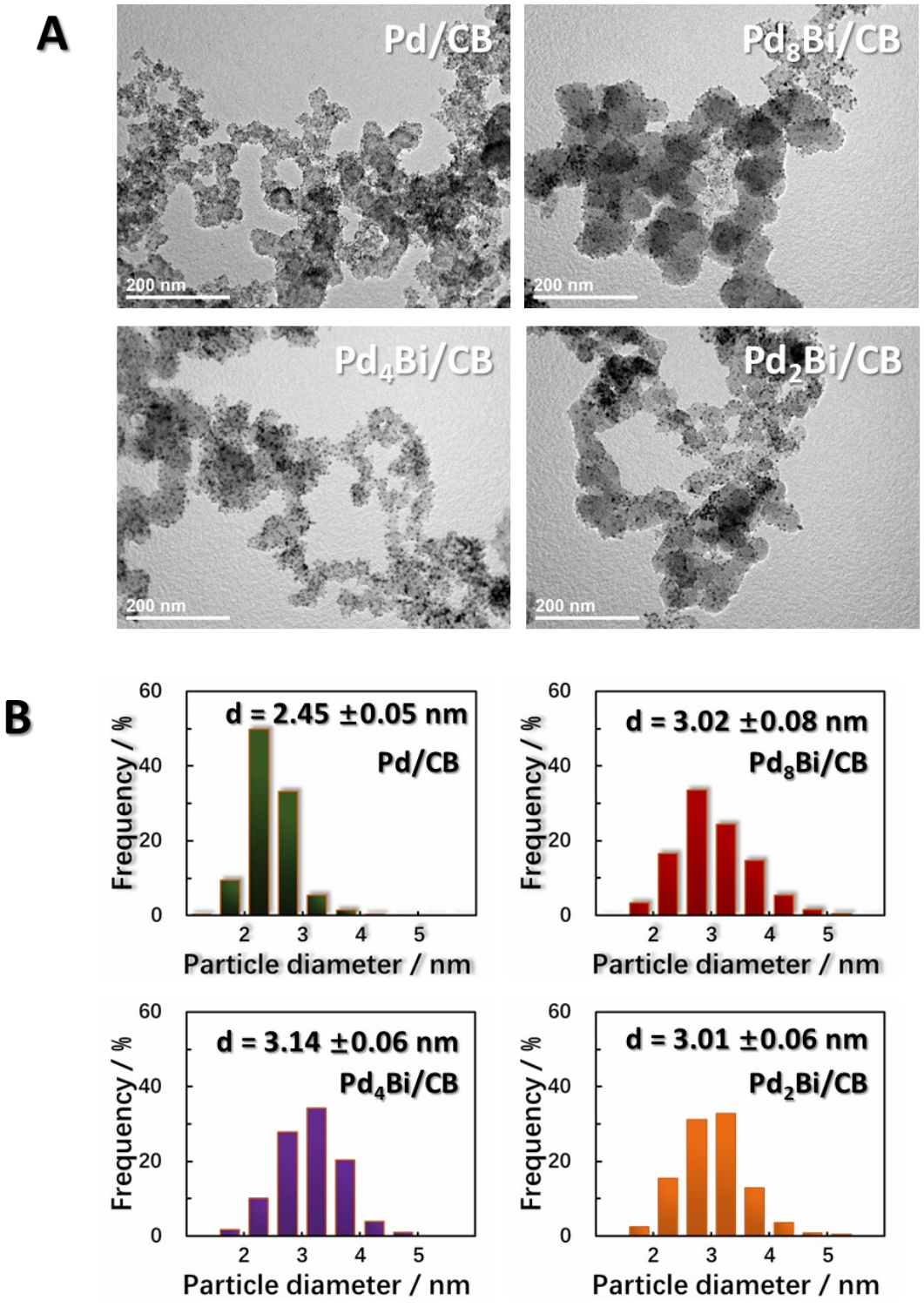

Fig. S1. High-magnification TEM images (A), the histograms of particle size distributions (B) of Pd/CB and Pd_XBi/CB nanocomposites.

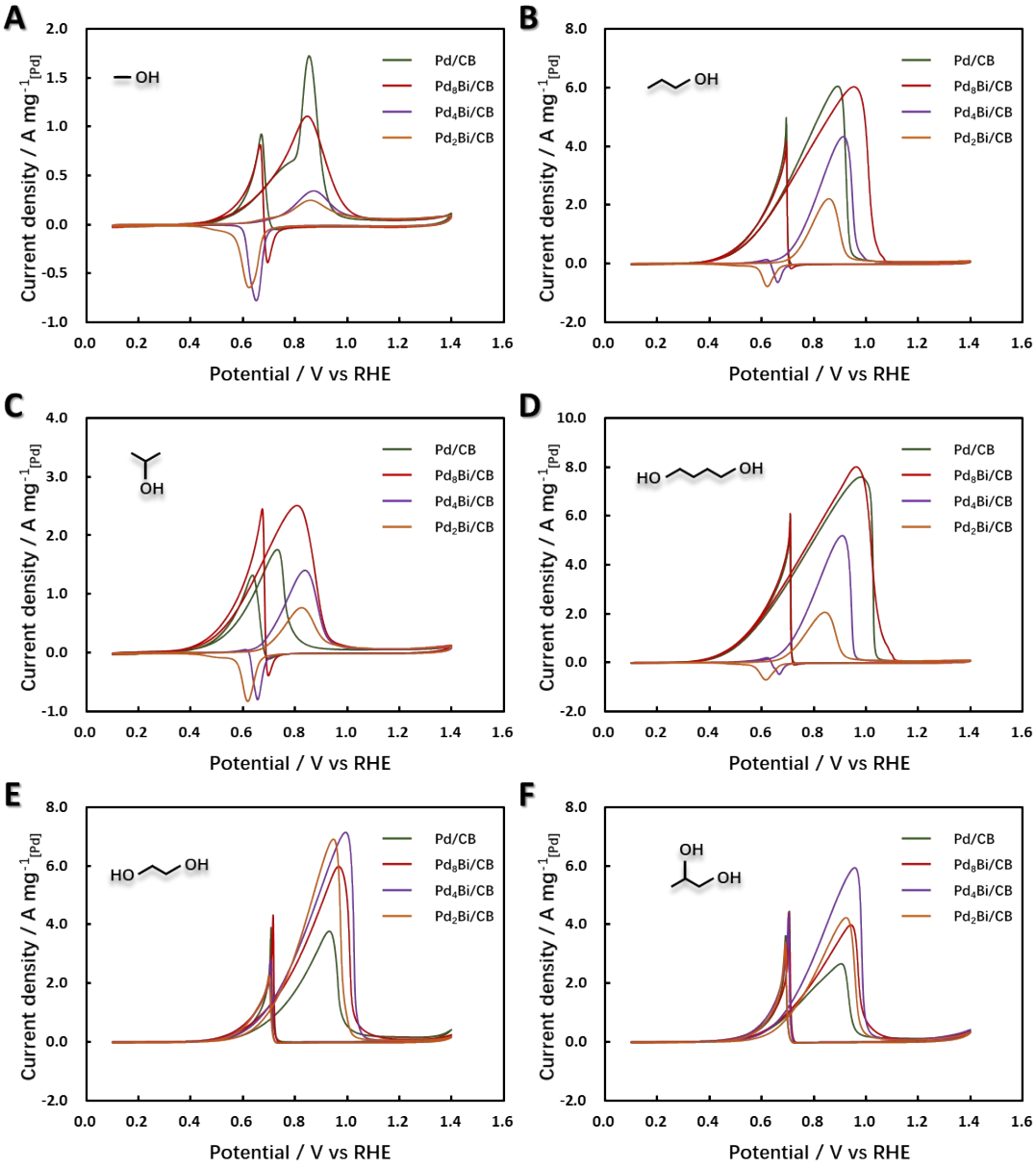

Fig. S2. CV curves recorded for the oxidation of different alcohols (1.0 M) in 1.0 M NaOH solutions (scan rate = 50 mV/s).

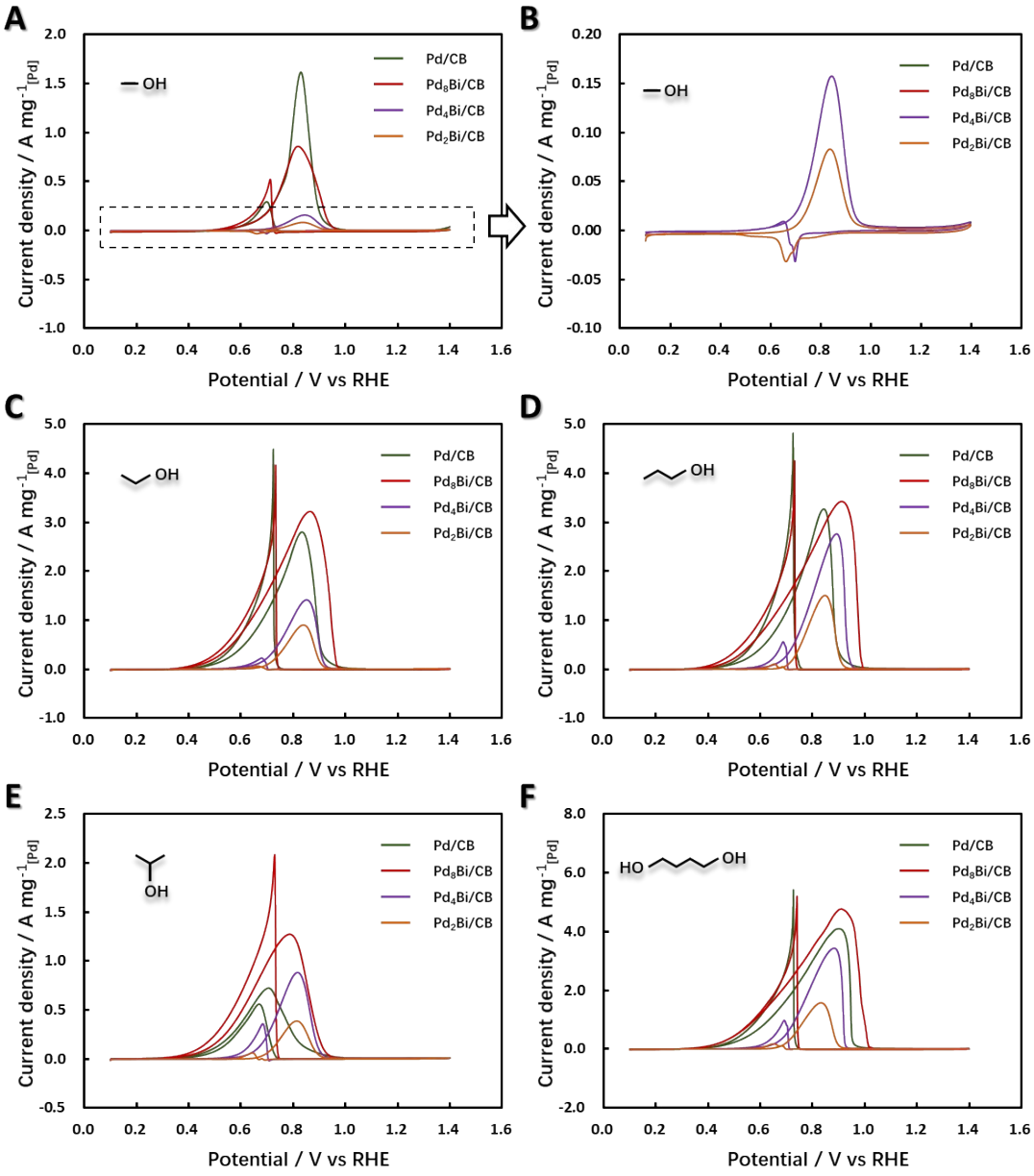

Fig. S3. CV curves recorded for the oxidation of different alcohols (1.0 M) in 1.0 M NaOH solutions (scan rate = 2 mV/s).

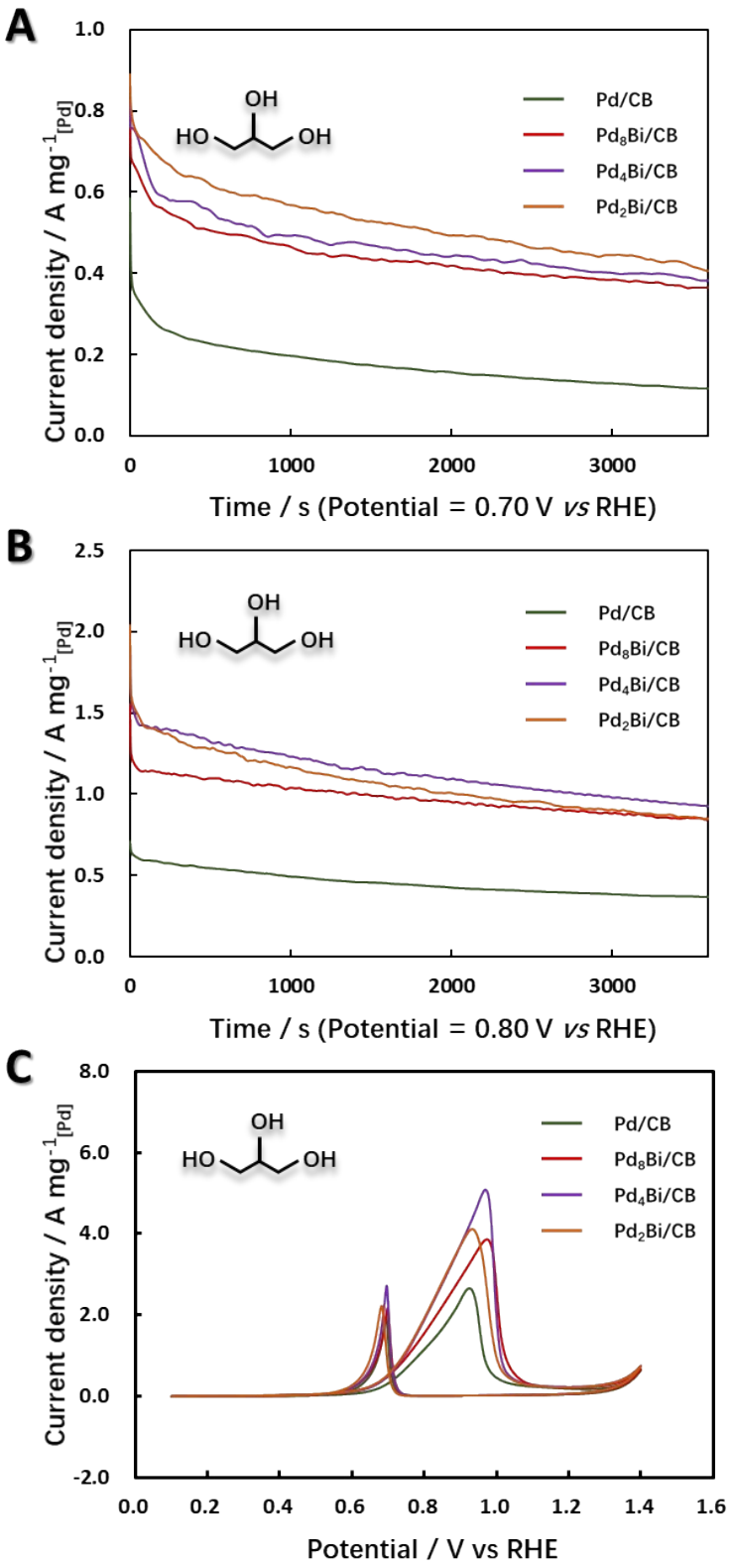

Fig. S4. Chronoamperometric curves at the potential of 0.70 V (A) and 0.80 V (B) recorded in 1.0 M glycerol + 1.0 M NaOH solution. CV curves of corresponding samples recorded after chronoamperometric test (C).