Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Pd-P nanoparticles supported on P_xO_y-incorporated carbon nanotubes for enhanced methanol oxidation in alkaline medium

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1. Experimental

1.1 preparation of Pd-P/PSCNTs、Pd-P/LPCNTs

Pristine carbon nanotubes (PSCNTs) were purchased from Pyrograf Products Inc. (Ohio, USA). LPCNTs were obtained by heating 50 mg OCNTs with 0.663 g sodium hypophosphite (NaH_2PO_2) at 600 °C under He gas.

Sodium citrate (0.22 g) was dissolved in water (10 mL), and a solution of $PdCl_2$ (2.66 mL, 0.056 M) in 0.27 M aqueous NaCl was added. The pH value was adjusted to 10 using 0.1 M sodium hydroxide, followed by addition of PSCNTs or LPCNTs (60 mg). After 30-min sonication, aqueous NaH_2PO_2 (10 mL, 0.1 M) was dropwise added to the slurry under vigorous stirring at a rate of 0.5 mL/min. After being continuously stirred at 80 °C for 4 h under reflux, the resulting suspension was filtered, and the solids were washed with distilled water and vacuum-dried at 70 °C for 7 h to obtain Pd-P/PSCNTs or Pd-P/LPCNTs with 20 wt.% Pd loading theoretically.

1.2 Preparation of Pd/PCNTs and Pd/OCNTs

242.08 μL $Pd(NO_3)_2$ (Sigma-Aldrich) were added to 10 mL of ethanol containing 50 mg PCNTs or OCNTs under sonication. The solvent was then removed through magnetic stirring at 45 °C. Finally, the collected powder was annealed in a tube furnace at 250 °C under a He/H_2 atmosphere to produce Pd/PCNTs and Pd/OCNTs catalysts with 20 wt.% Pd loading theoretically.

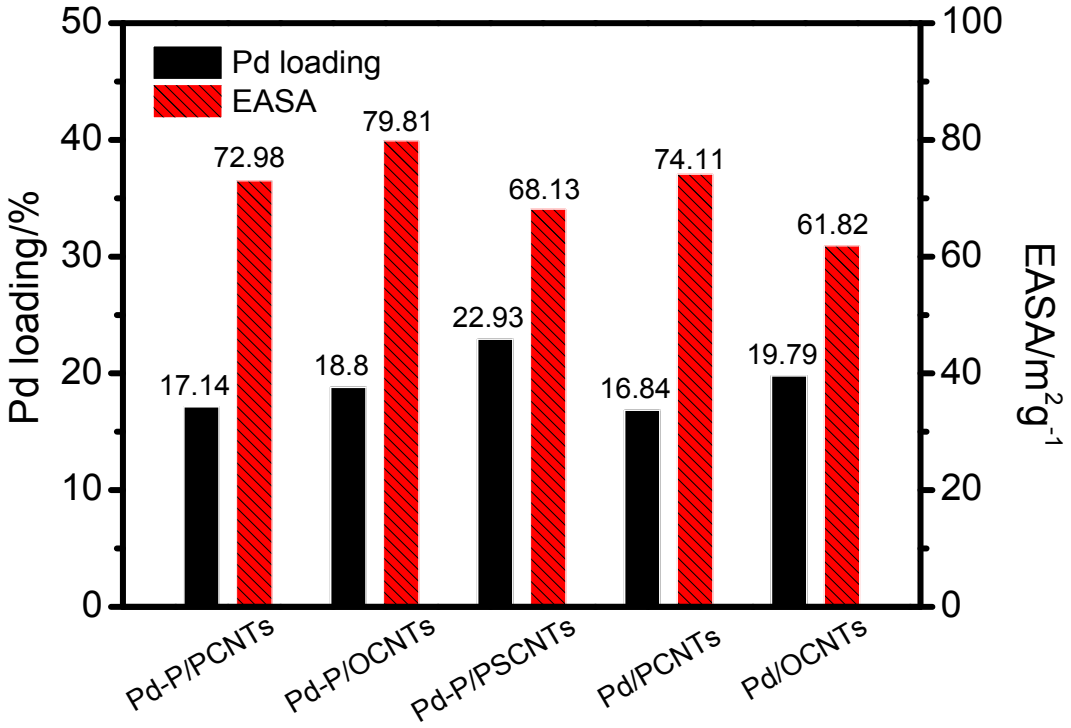

Figure S1. Histogram of Pd loadings and EASAs of Pd-P/PCNTs, Pd-P/OCNTs, Pd-P/PSCNTs, Pd/PCNTs and Pd/OCNTs.

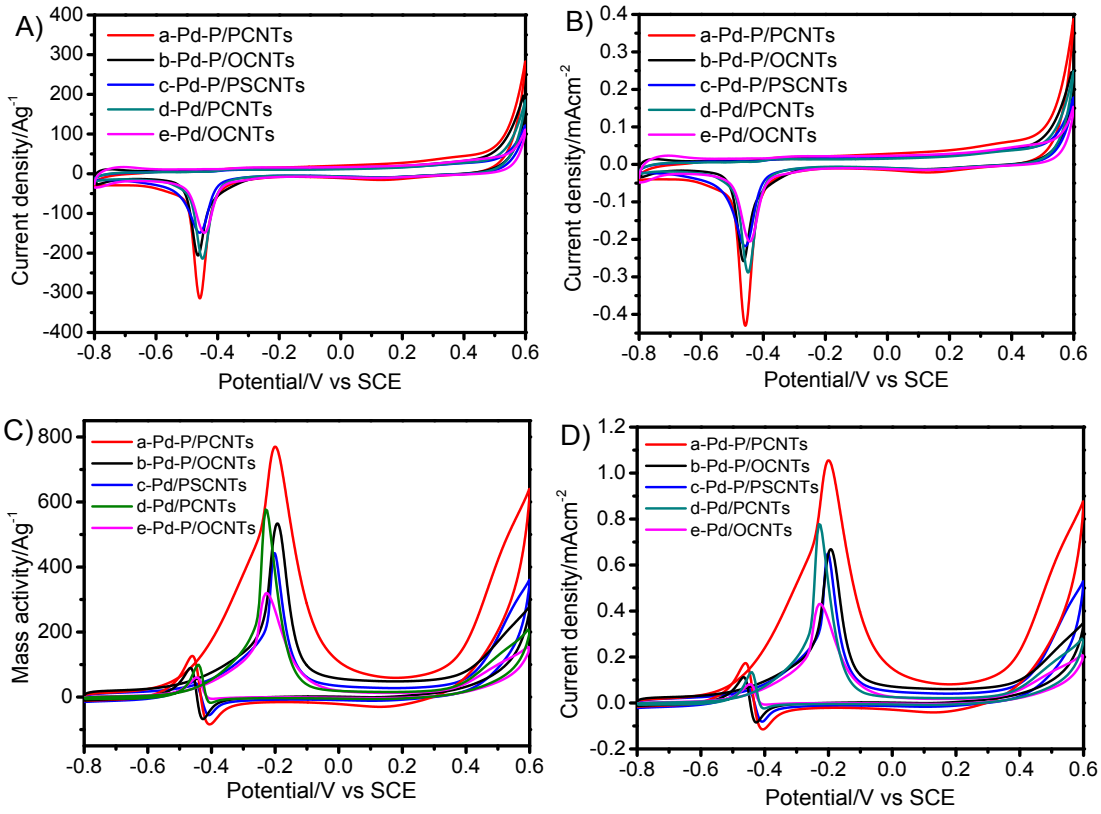

Figure S2. CV curves of (a) Pd-P/PCNTs, (b) Pd-P/OCNTs, (c) Pd-P/PSCNTs, (d) Pd/PCNTs and (e) Pd/OCNTs in 0.5 M NaOH with mass-normalized current (A) and EASA-normalized current (B); in 0.5 M NaOH + 1 M CH_3OH with mass-normalized current (C) and EASA-normalized current (D) at a scan rate of 50 mV s^{-1}.

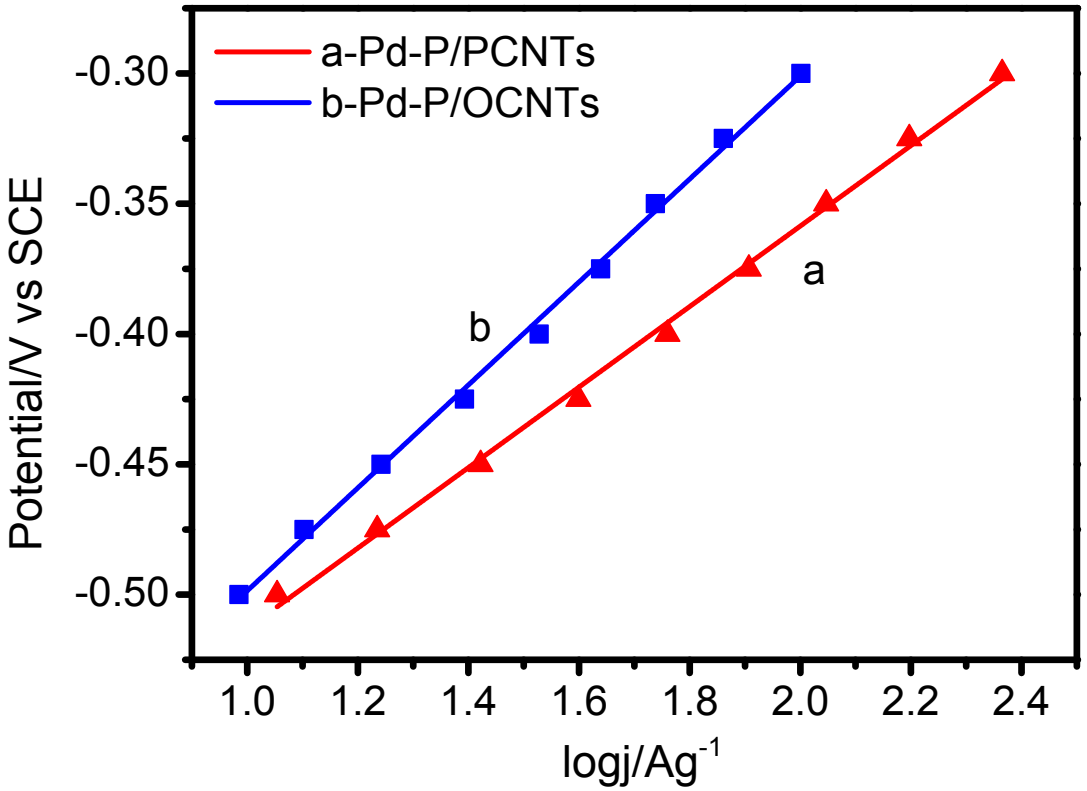

Figure S3. Tafel plots for methanol oxidation on (a) Pd-P/PCNTs and (b) Pd-P/OCNTs in 0.5 M NaOH + 1 M CH_3OH solution.

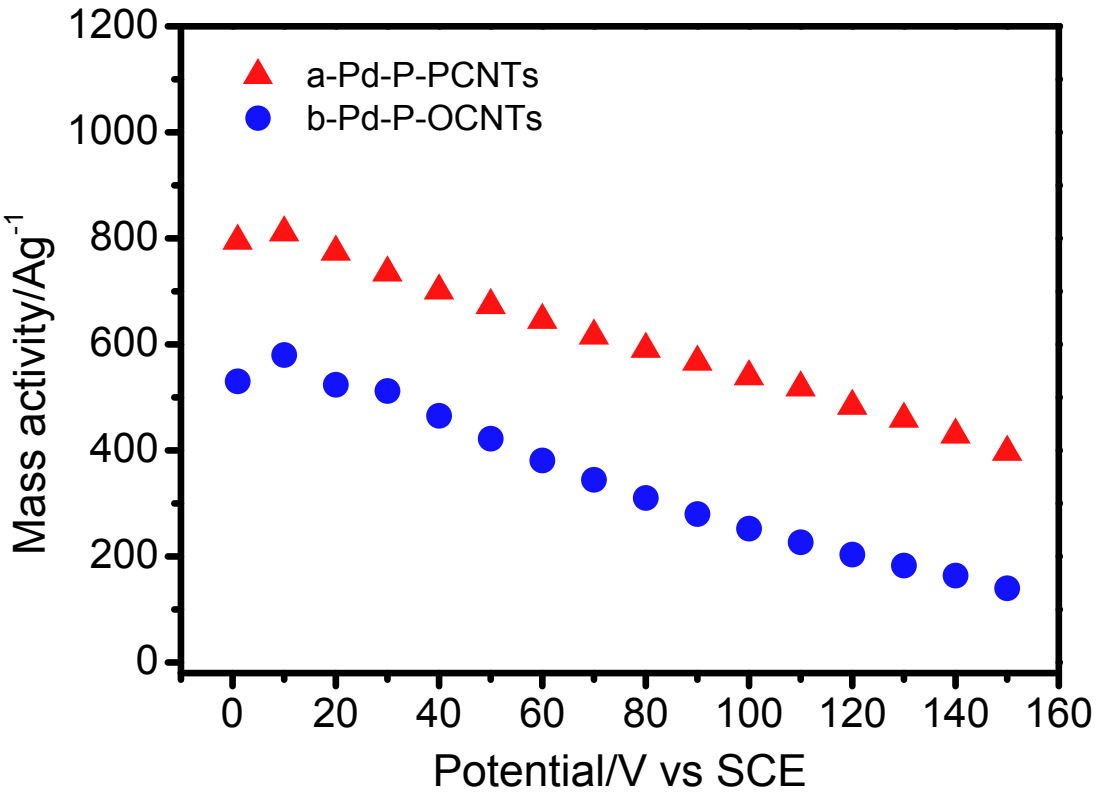

Figure S4. Scatter plot of forward peak current density vs. cycle number in 0.5 M NaOH + 1 M CH_3OH of (a) Pd-P/PCNTs and (b) Pd-P/OCNTs.

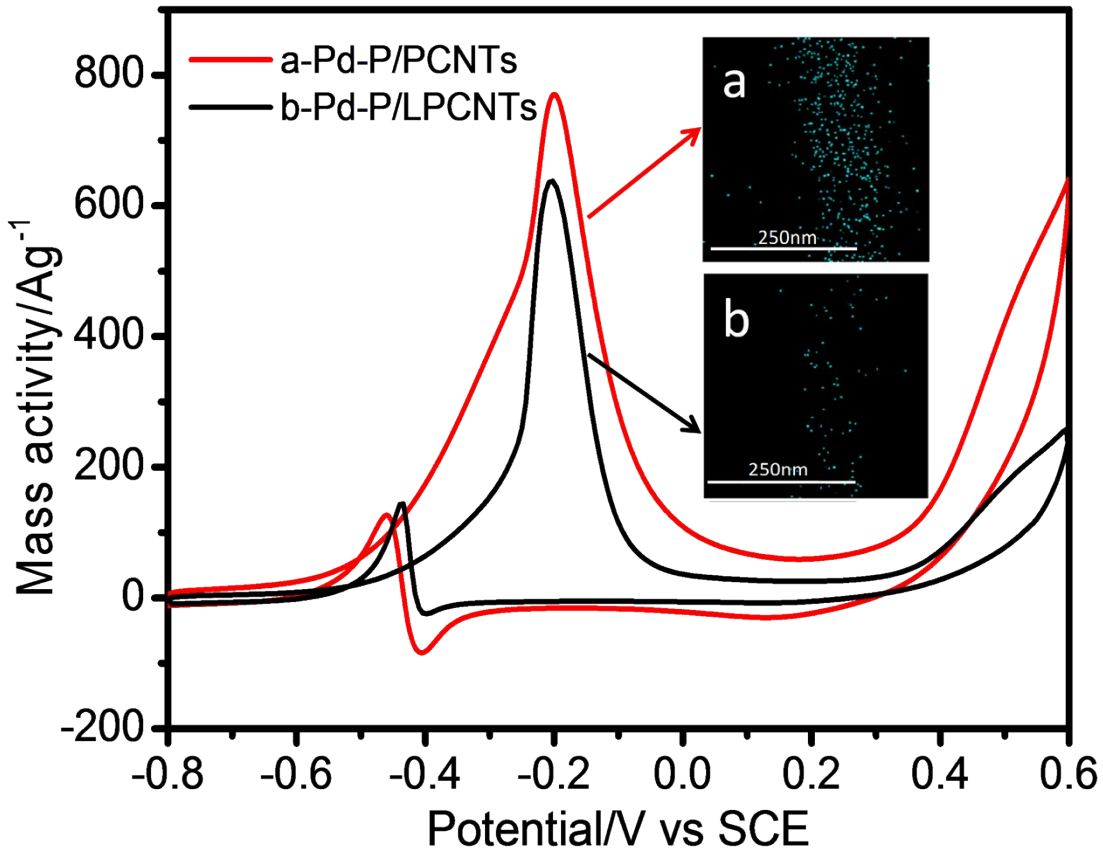

Figure S5. CV curves of Pd-P/PCNTs and Pd-P/LPCNTs in 0.5 M NaOH + 1 M CH_3OH at a scan rate of 50 mV s^{-1} with the insets of EDX mapping of P of (a) PCNTs and (b) LPCNTs.

Table S1. Comparison of various catalysts with EASA, mass activity and specific activity in this study and reported Pd-based catalysts.

Working Electrode	Testing Conditions	EASA ($cm^2\ mg^{-1}$)	Mass Activity ($mA\ mg^{-1}$)	Specific Activity ($mA\ cm^{-1}$)	Reference
Pd-P/PCNTs	0.5M NaOH 1M CH_3OH	729.8	772.67	1.06	This work
Pd-P/OCNTs	0.5M NaOH 1M CH_3OH	798.1	533.51	0.67	This work
Pd/PCNTs	0.5M NaOH 1M CH_3OH	741.1	574.02	0.77	This work
Ni@Pd/MWCNTs	0.5M NaOH 1M CH_3OH	1762.0	770.7	0.44	[1]
Pd-Ag(1:1)/CNTs	1M KOH 1M CH_3OH	$1.14 cm^{-2}$	—	0.950	[2]
8nm Pd-Ni-P NPs	0.5M KOH 1M CH_3OH	629.0	360.00	0.57	[3]
17nm Pd-Ni-P NPs	0.5M KOH 1M CH_3OH	283.0	170.00	0.60	[3]
Pd_2/P_1	1M KOH 1M CH_3OH	507.01	844.74	1.67	[4]
Pd/polypyrrole--graphene	0.5M NaOH 1M CH_3OH	418.0	359.8	0.86	[5]

Reference

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