Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Directed Self-Assembly Pathways of Three-dimensional Pt/Pd Nanocrystal Superlattices Electrocatalysts for Enhanced Methanol Oxidation Reaction

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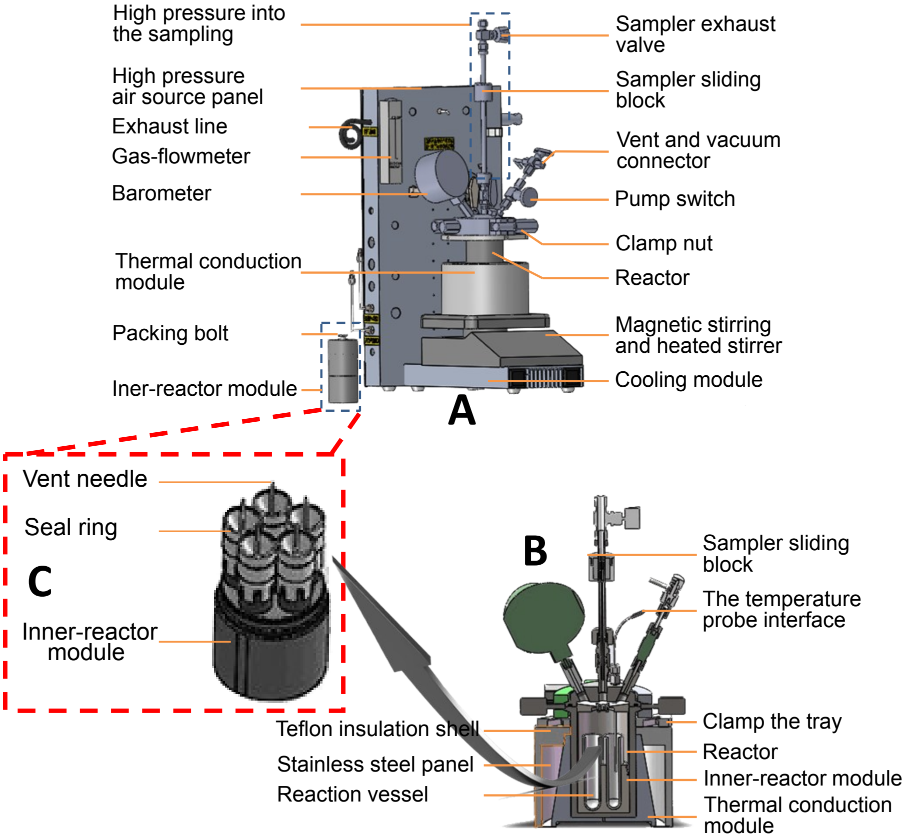
Table S1. EXAFS Fitting Results of 3D Pt/Pd NSLs-WPAS and 3D Pt/Pd NSLs-SM[a]

Samples	Pt-Pt		D. W.	ΔE_0 (eV)
	R (Å)	CN		
Pt foil	2.77±0.00	12	0.005±0.000	7.7±0.4
3D Pt/Pd NSLs-WPAS	2.75±0.01	8.2±1.1	0.007±0.001	8.6±1.0
3D Pt/Pd NSLs-SM	2.74±0.01	7.1±0.8	0.007±0.001	8.2±0.9

[a]R: distance; CN: coordination number; D. W.: Debye−Waller factor.

Table S2. The barriers E_a (eV), reaction energies $\Delta_r E$ (eV) and rate constant k (s^{-1}) for all the elementary reactions of the methanol oxidation reaction (MOR) on $Pt_4Pd(111)$-WPASA and $Pt_4Pd(111)$-SM surfaces.

Surface reactions	$Pt_4Pd(111)$-WPAS			$Pt_4Pd(111)$-SM		
	E_a	$\Delta_r E$	k	E_a	$\Delta_r E$	k
$CH_3OH \rightarrow CH_3O + H$	0.54	0.19	1.33×10^{3}	1.18	0.26	2.50×10^{-8}
$CH_3O \rightarrow CH_2O + H$	0.45	-0.31	1.40×10^{5}	0.59	-0.41	8.92×10^{2}
$CH_2O \rightarrow CHO + H$	0.56	0.25	1.44×10^{3}	0.41	-0.58	3.02×10^{5}
$CHO \rightarrow CO + H$	0.83	-0.93	3.41×10^{-2}	0.71	-1.17	1.15×10^{1}
$CO + 2OH \rightarrow CO_{2(g)} + H_2O$	0.51	-0.84	1.82×10^{3}	0.38	-0.85	7.85×10^{5}



Scheme S1. (A) Over-view diagram, (B) section-view diagram, and (C) inner-reactor module diagram of the Wattecs Parallel Autoclave System (WPAS). The WPAS synthetic technique holds the advantages of high temperature and high pressure and allows the constant stirring under a nitrogen and argon gas protecting atmosphere in comparison with normal solvothermal synthetic approach. [1]

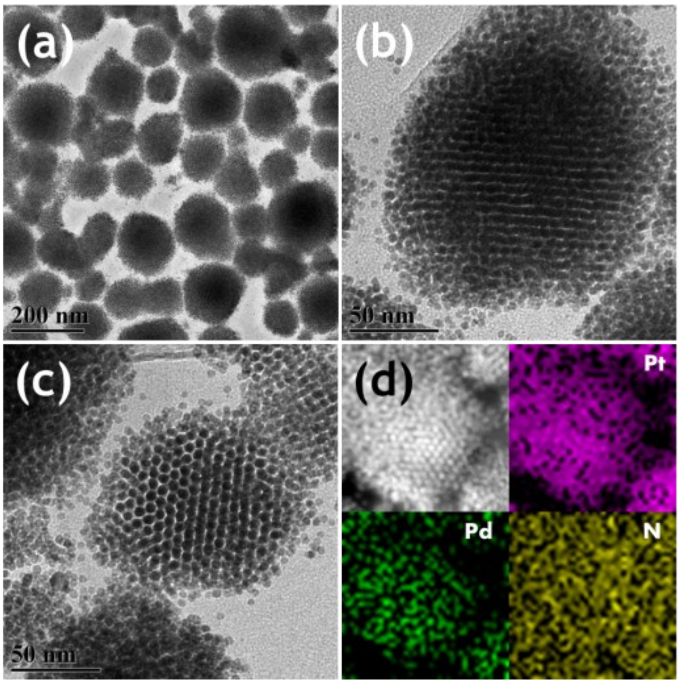


Fig. S1. TEM images of 3D Pt/Pd NSLs-WPAS synthesized with a theoretical molar ratio of Pt:Pd at 1:1.

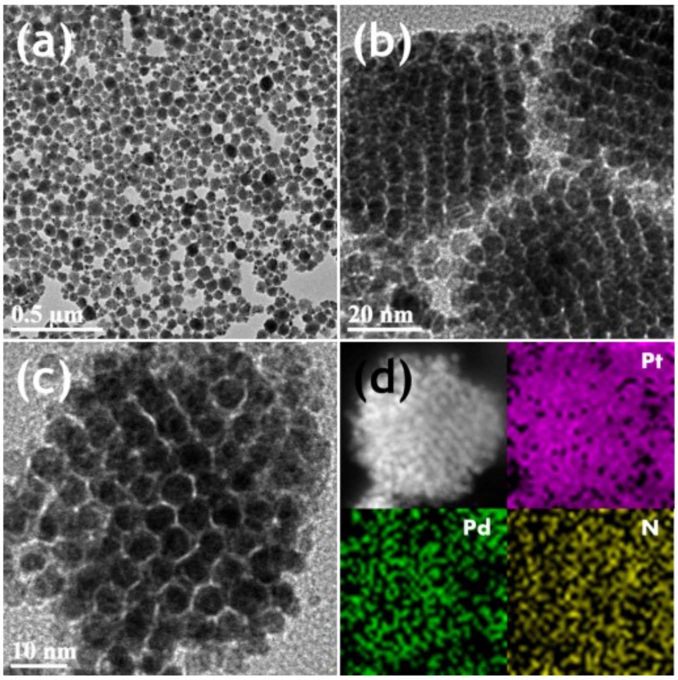


Fig. S2. TEM images of 3D Pt/Pd NSLs-WPAS synthesized with a theoretical molar ratio of Pt:Pd at 1:3.

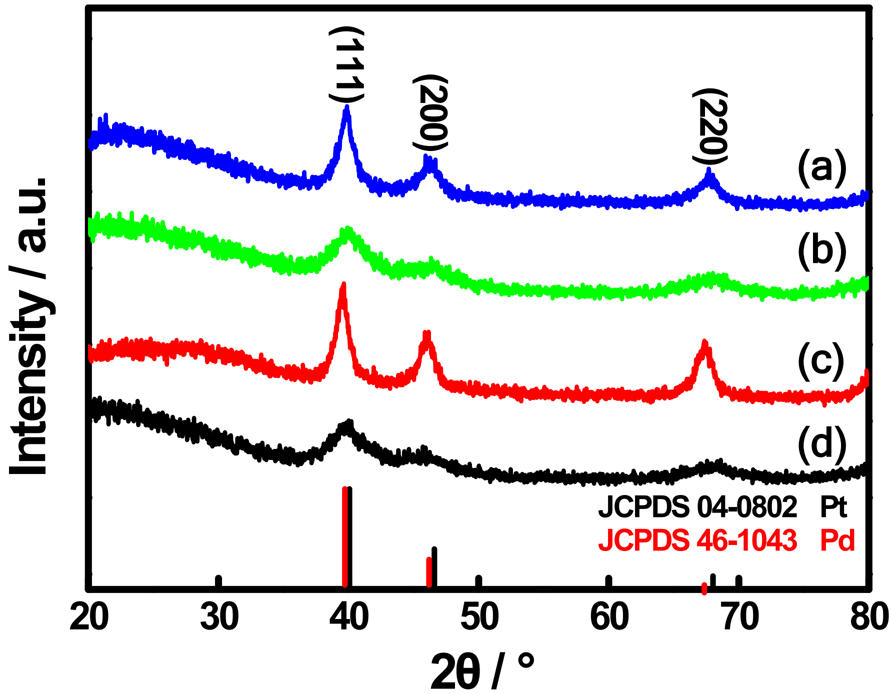


Fig. S3. The XRD patterns of (a) 3D Pt/Pd NSLs-WPAS, (b) 3D Pt/Pd NSLs-SM, (c) Pd@Pt core-shell NCs, and (d) Pt/Pd monodispersed NCs.

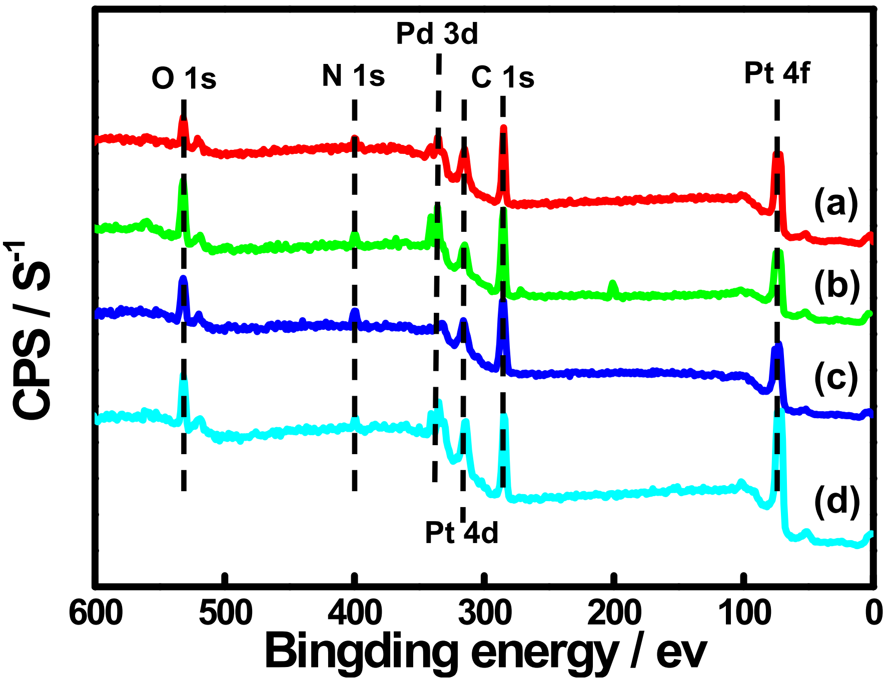


Fig. S4. XPS survey spectra of (a) 3D Pt/Pd NSLs-WPAS, (b) 3D Pt/Pd NSLs-SM, (c) Pd@Pt core-shell NCs, and (d) Pt-Pd monodispersed NCs.

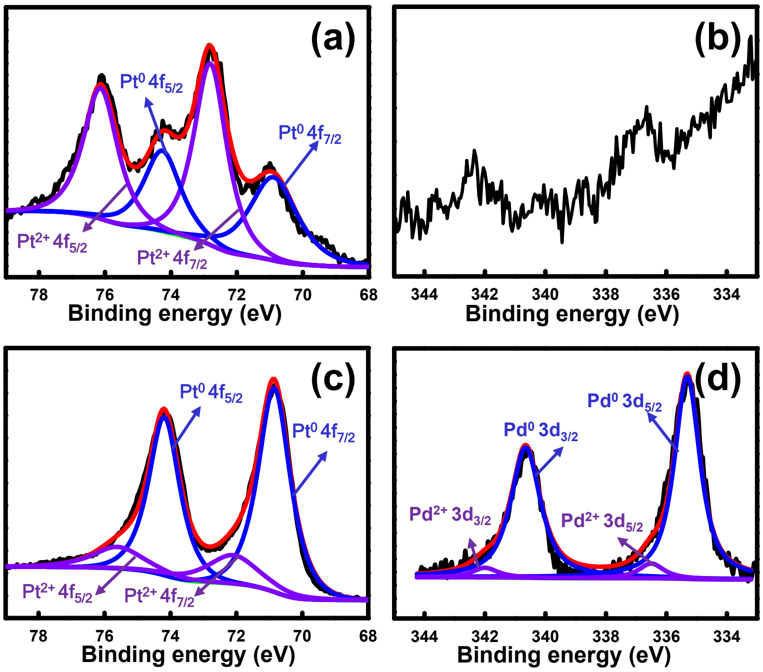


Fig. S5. XPS spectra of (a and c) Pt 4f and (b and d) Pd 3d of (a and b) Pd@Pt core-shell NCs and (c and d) Pt/Pd monodispersed NCs.

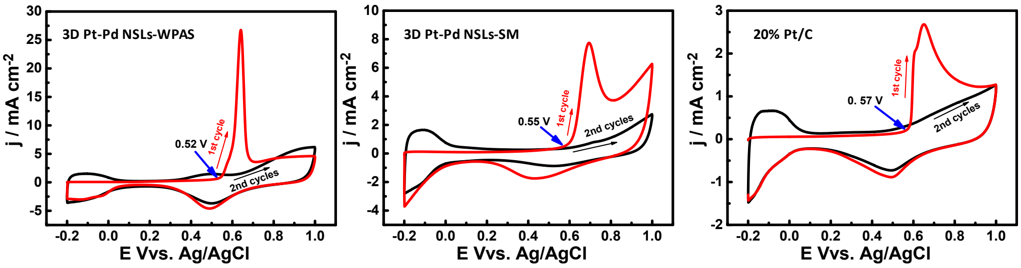


Fig. S6. CO-stripping voltammograms over 3D Pt/Pd NSLs-WPAS, 3D Pt/Pd NSLs-SM, and the commercial Pt/C electrocatalysts in a CO-saturated 0.5 M H_2SO_4 solution at a scan rate of 50 mV s^{-1}.

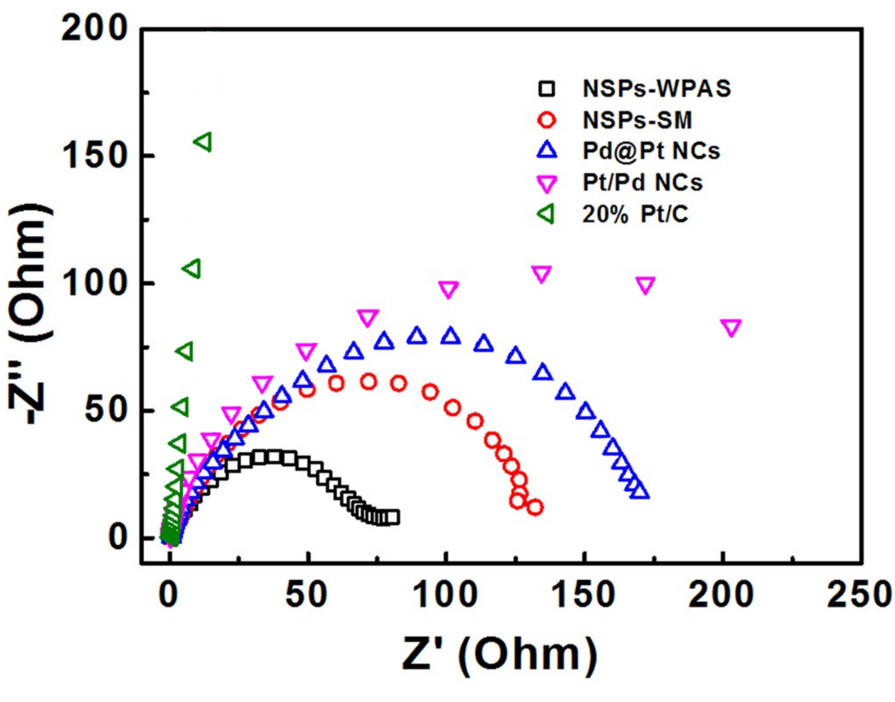


Fig. S7. Electrochemical impedance spectra of different catalysts measured in N_2-saturated 0.5 M H_2SO_4 + 1.0 M CH_3OH solution.

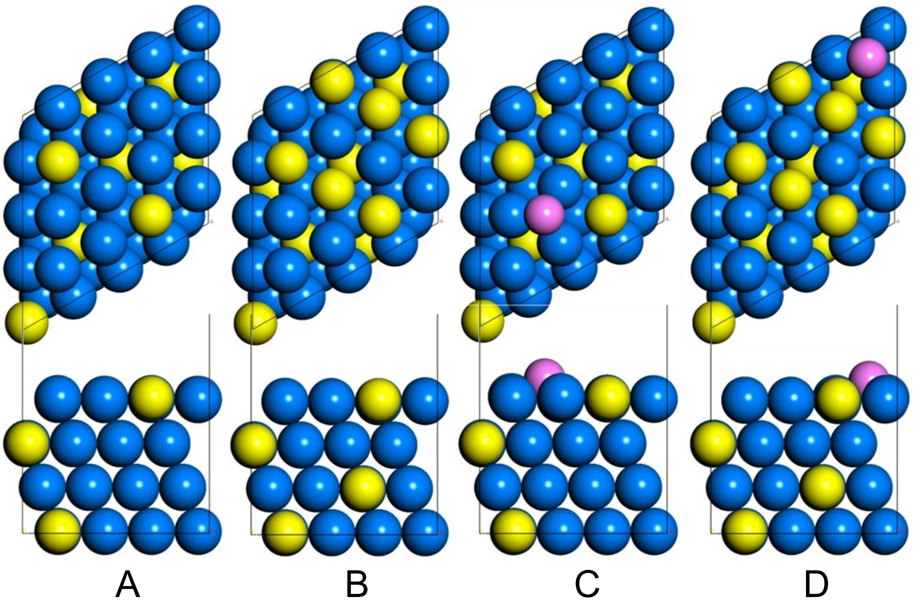


Fig. S8. The top and side views for (a) $Pt_4Pd(111)$-WPAS and (b) $Pt_4Pd(111)$-SM surfaces, as well as the adsorption structures of atomic N on the two models (c) N/WPAS and (d) N/SM (the Pt, Pd and N atoms in blue, yellow and pink, respectively).

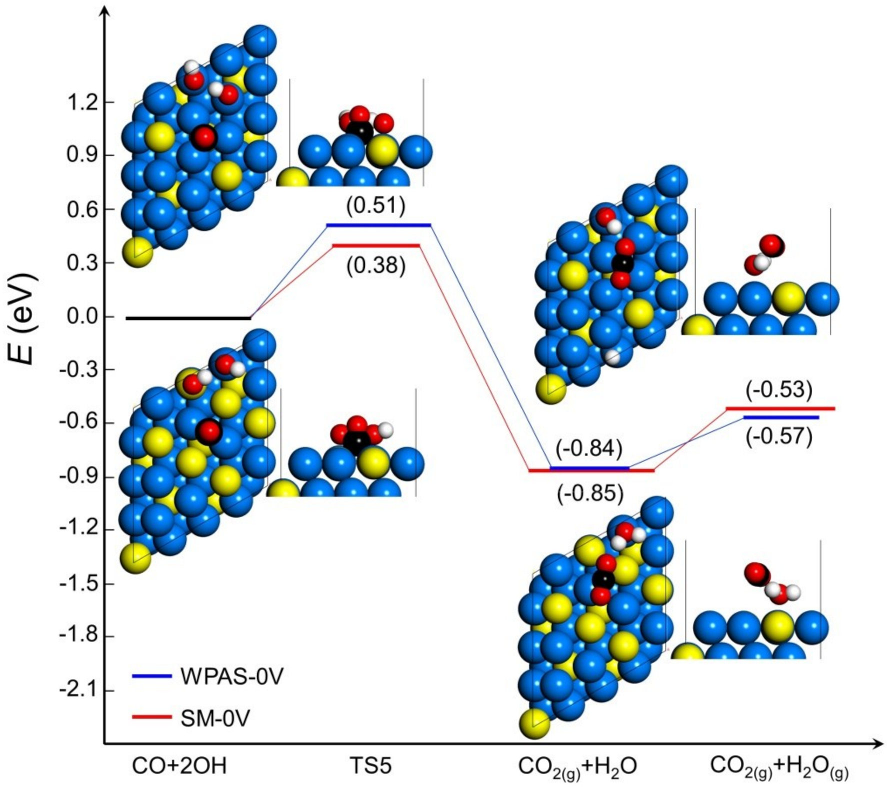


Fig. S9. Intermediate structures and corresponding energies for elementary steps of the reaction CO + 2OH → CO_2 + H_2O. TS, transition state.

References:

1. G. Xu, J. Liu, B. Liu, X. Gong, S. Wang, Q. Wang and J. Zhang, *CrystEngComm*, 2017, **19**, 7322-7331.