Supporting Information

Enhanced Methanol Electrooxidation at Pt skin@PdPt Nanocrystals

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Table S1. Catalysts loading and comparison with literature

S. No.	Materials	Metal loading on carbon black (wt%)	Pt loading on GC (μg/cm²)	Total metal loading on GC (μg/cm²)	References
1.	PtCo	20	8-20	20-52	(1)
2.	PdCu	20	-	14-28	(2)
3.	Pt-on-Pt dendrites	100 (No carbon support)	NA	84	(3)
4.	Au Islands on Pt-Ni	20	NA	2.55 – 5.1	(4)
5.	Pt and PtRu	20	NA	15-20	(5)
6.	PdPt/GO	2.23	1.86	11.4	(6)
7.	CoNiPt/MWCNTs	17	NA	24	(7)
8.	Pt/C	20	18.5	NA	(8)
9.	Rhombic PtCu nanoframes	NA	13.52	NA	(9)
10.	**Present Pt@PdPt**	**36.25**	**7.48**	**17.11**	**Present work**

The Pt loading on the glassy carbon should be 7-30 $\mu g_{Pt}.cm^{-2}$ for catalysts having concentrations of 10-50 wt% Pt. Thin-films (on the order of 200 nm) are ideal and preferable, since thicker films may amplify the mass-transport limitations through the catalyst layer. In present work, we have employed the catalysts loading in the ideal limit mentioned above, which is also a standard protocol adopted to make homogeneous and thin films.

References

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S1. PdPt (Prepared in single step; Composition of $Pd_{72}Pt_{28}$)

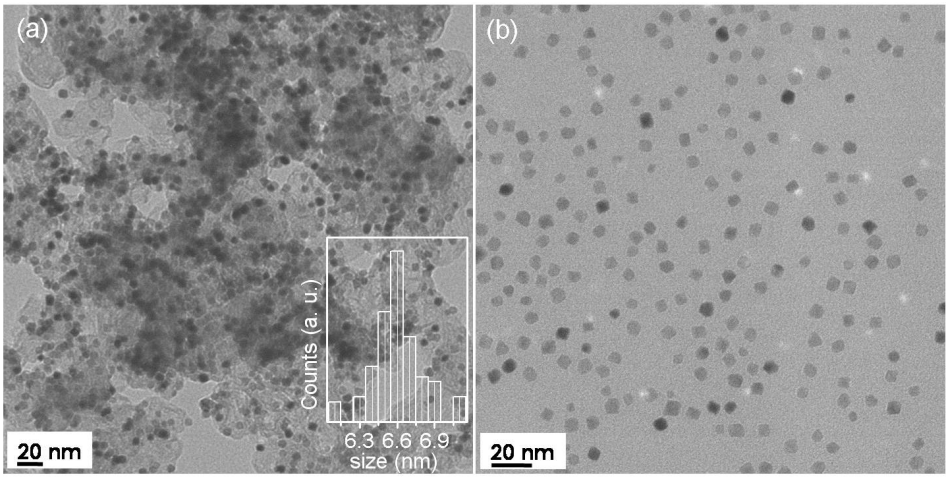

Figure S1. TEM images of (a) PdPt supported on carbon (b) PdPt prepare in single step with a composition of **$Pd_{72}Pt_{28}$** (determined from ICP-AES); inset of (a) shows the particle size distribution of 6.6±0.5 nm.

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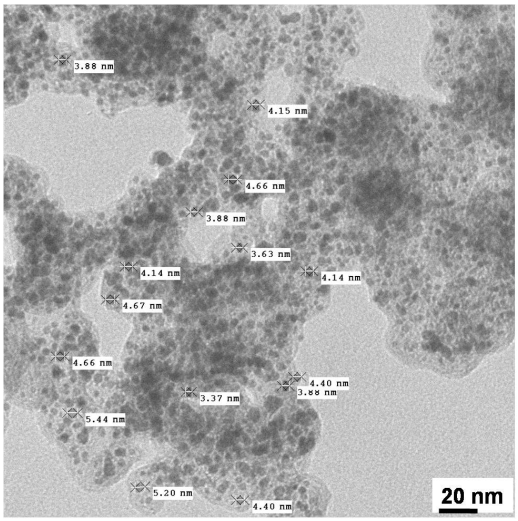
Table S2: Comparative particle size, atomic ratios, metal loading, ECSA and MOR activities of all catalyst normalized by total active metal loading

Catalyst	Particle Size (nm)	Empirical formula (Atomic ratio)	Metal loading (Pt+Pd) on carbon black (wt%)	Pt loading on GC ($\mu g/cm^2$)	Total metal (Pd+Pt) loading on GC ($\mu g/cm^2$)	ECSA (m^2/g)	Mass activity (mA/mg_{Pt})	Mass activity (mA/mg_{Pt+Pd})
Pt1@PdPt	7.5±0.5	$Pd_{71}Pt_{29}$	35.29	6.91	16.31	90	1525	647
Pt2@PdPt	6.9±0.3; 7.7±0.3	$Pd_{70}Pt_{30}$	36.25	7.48	17.11	82	1952	859
PdPt	6.6±0.5	$Pd_{72}Pt_{28}$	35.24	6.22	15.77	48	380	160
RuPt Comm	1.00 to 5.00	$Ru_{79}Pt_{21}$	Pt+Ru = 49.4	14.26	21.68	52	247	163



TEM image of commercial RuPt/C (comprising Pt = 32.5 wt% and Ru = 16.9 wt% with a total of 49.4 wt% metal loading) showing heterogeneous particle size distribution.

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S2. Comparison between Pt-OH_{ads} and Pd-OH_{ads} surface

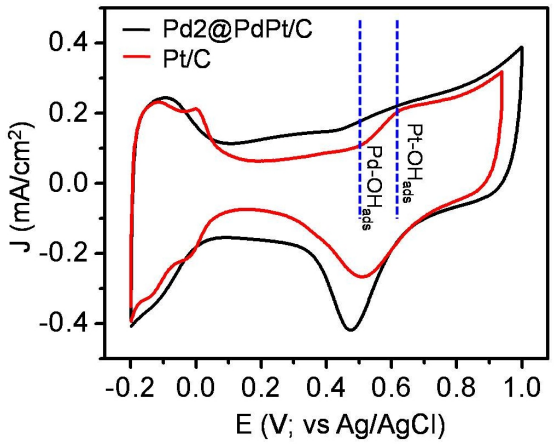

Figure S2. Comparative voltammograms revealing obvious changes in the Pt-OH_{ads} region (~0.6 V) after bimetallic combination; Pd-OH_{ads} is formed at a lower potential than Pt-OH_{ads} clearly indicating that the Pd is more vulnerable to oxidation changes

S3. Methanol electrooxidation for Pt black

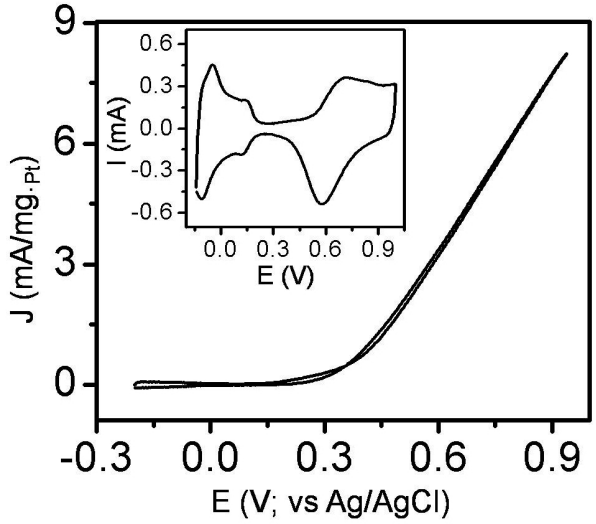

Figure S3. MOR of Pt black; inset showing CV in absence of MeOH at 20 mV/s.

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S4. Stability tests:

Electrocatalytic stability of Pt@PdPt/C for various alcohol electrooxidations, the catalysts were cycled between -0.25 and 1.0 V up to 5000 cycles under similar conditions of 0.1 M $HClO_4$ and 0.1 M Methanol/ethanol/Ethylene glycol.

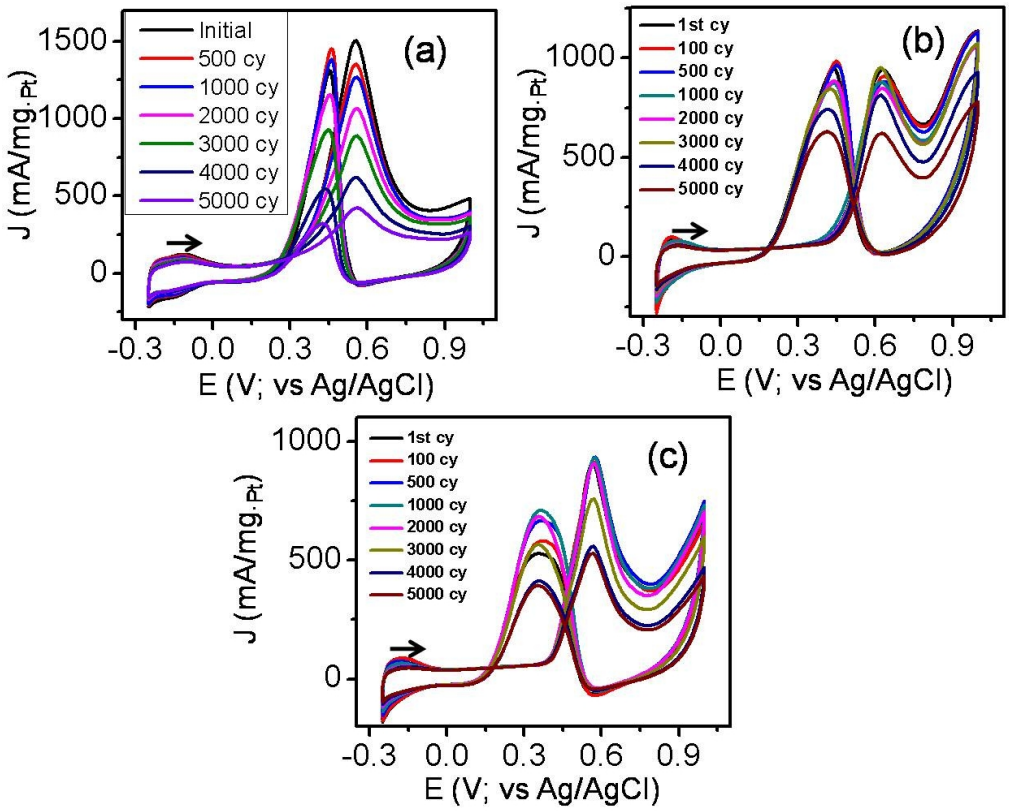

Figure S4. Stability test for (a) Pt1@PdPt for MOR (b) EOR using Pt2@PdPt (c) EGOR using Pt2@PdPt.

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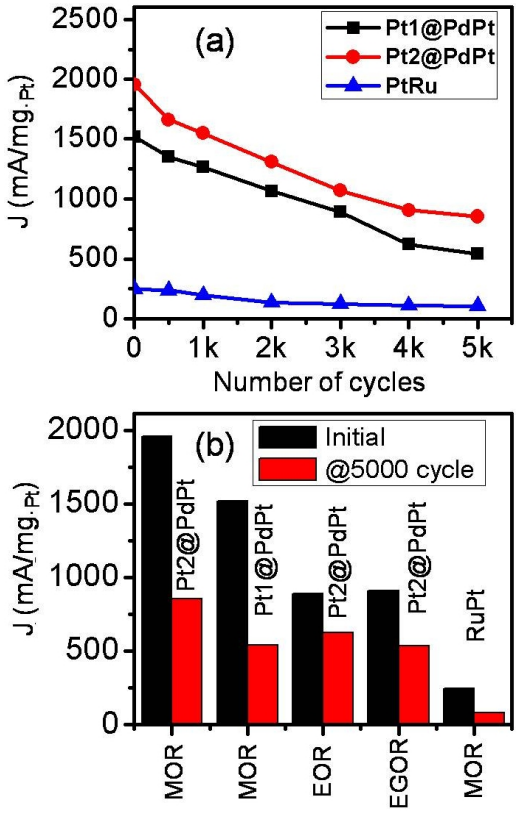

Figure S4. (a) Comparative stability tests of Pt2@PdPt/C and Pt1@PdPt/C with RuPt/C (b) histogram representing comparative activities before and after 5000 cycles for all electrooxidation reactions.

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