Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Ultrafine PdO_x nanoparticles on spinel oxides by galvanic displacement for catalytic combustion of methane

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Content

Experimental serction

Pd-$NiCo_2O_4$ without H_2 treatment (denoted as NR-Pd/$NiCo_2O_4$): 200 mg $NiCo_2O_4$ was added into the bottle of U tube with flowing Ar gas at 200 °C for 30 min. The rest of the synthetic procedure was similar to that used for the synthesis of the GD-Pd/$NiCo_2O_4$.

$NiCo_2O_4$ with H_2 treatment (denoted as RE-$NiCo_2O_4$): 200 mg $NiCo_2O_4$ was added into the bottle of U tube with flowing 5% H_2/Ar at 200 °C for 30min. When the temperature reduces under 100 °C, then switch to pure Ar gas. After cooling to room temperature, 10 ml HNO_3 solution (pH = 1) was quickly injected into U tube with continual flowing Ar and magnetic stirring at 250 rmp/min for 12 h. The rest of the synthetic procedure was similar to that used for the synthesis of the GD-Pd/$NiCo_2O_4$.

Kinetic data were collected under kinetics control regime (methane conversion < 10%). The reaction condition: 20 mg catalysts were physically mixed with 500 mg quartz sand (40–60 mesh) at a flow gas rate of 100 ml/min. The reaction rates of CMC were calculated using Eq (1):

$$R(mmol\ h^{-1} g_{cat}^{-1}) = \frac{X_f G C}{22.4 W_{cat}} \quad (1)$$

Where X_f is the concentration of CH_4 and G is the gas flow rate (ml/h). C is the methane conversion and W_{cat} is the weight of the spinel oxides catalysts (g). And the reaction rates equation:

$$R = A[CH_4]^a[O_2]^b$$

When the methane conversion is very low (< 10%) at 250 °C, the A is constant.

$$lgR = lgA + alg[CH_4] + blg[O_2]$$

When the concentration of O_2 is fixed, the correlation between lgR and lg $[CH_4]$ is close to linear. Then, the reaction orders of CH_4 over the GD-Pd/$NiCo_2O_4$ and $NiCo_2O_4$ can be estimated by plotting lgR vs lg$[CH_4]$.

Tables

Table S1

XPS data measured for $NiCo_2O_4$ and $Pd/NiCo_2O_4$ catalysts.

Catalysts	Binding enery (eV)			Surface element composition		
	Pd $3d_{5/2}$	Ni $2p_{3/2}$	Co $2p_{3/2}$	Pd^{4+}/Pd^{2+}	Ni^{2+}/Ni^{3+}	Co^{2+}/Co^{3+}
$NiCo_2O_4$	-	854.8	779.6	-	0.33	1.13
Pd(3nm)/$NiCo_2O_4$	337.0	854.7	779.6	0.50	0.49	2.94
WI-Pd/$NiCo_2O_4$	337.2	854.7	779.5	0.53	0.50	2.77
GD-Pd/$NiCo_2O_4$	337.5	854.4	778.0	3.75	1.38	5.98

Table S2

Quantitative analysis of surface element composition from XPS spectra.

Catalysts	Pd	Co	Ni	O
$NiCo_2O_4$	0	17.26	9.52	73.22
Pd(3nm)/$NiCo_2O_4$	1.94	15.03	6.67	76.36
WI-Pd/$NiCo_2O_4$	2.38	15.16	6.83	71.14
GD-Pd/$NiCo_2O_4$	3.42	17.00	4.63	75.27

Table S3

Overview of activity of catalysts we prepared and ones from the reference.

Catalysts	Reaction conditions	T_{50}(ºC)	References
GD-4.4% Pd/$NiCo_2O_4$	1% CH_4; 99% Air, 24000 ml h^{-1} g^{-1}	235	This work
GD-4.4% Pd/$NiCo_2O_4$	1% CH_4; 99% Air, 300000 ml h^{-1} g^{-1}	305	This work
GD-4.4% Pd/$NiCo_2O_4$	1% CH_4; 10% H_2O; 89% Air, 60000 ml h^{-1} g^{-1}	280	This work
0.5Pd/Al_2O_3	1% CH_4; 22% O_2, 17000 ml h^{-1} g^{-1}	390	[1]
Pd@CeO_2/H-Al_2O_3	0.5% CH_4; 2% O_2, 200000 ml h^{-1} g^{-1}	280	[2]
1.97$Au_{0.45}$Pd/meso-Co_3O_4	2.5% CH_4; 20% O_2; 10% H_2O, 20000 ml h^{-1} g^{-1}	300	[3]
1%Pd-0.2%Pt/Ce/Al_2O_3	1.5% CH_4; 98.5% Air, 80000 h^{-1}	340	[4]
0.4%Pd/0.5NiO/Al_2O_3	1% CH_4; 99% Air, 30000 ml h^{-1} g^{-1}	310	[5]
1.1%Pt/3DOM CYZ	2% CH_4; 20% O_2, 30000 ml h^{-1} g^{-1}	434	[6]
2%Pd/Ba-Al_2O_3	500ppm CH_4; 5% H_2O; 8% O_2, 30000 h^{-1}	394	[7]
Au@PdO_x/Co_3O_4	0.2% CH_4; 10% H_2O; 10% O_2, 30000 ml h^{-1} g^{-1}	360	[8]

Figures

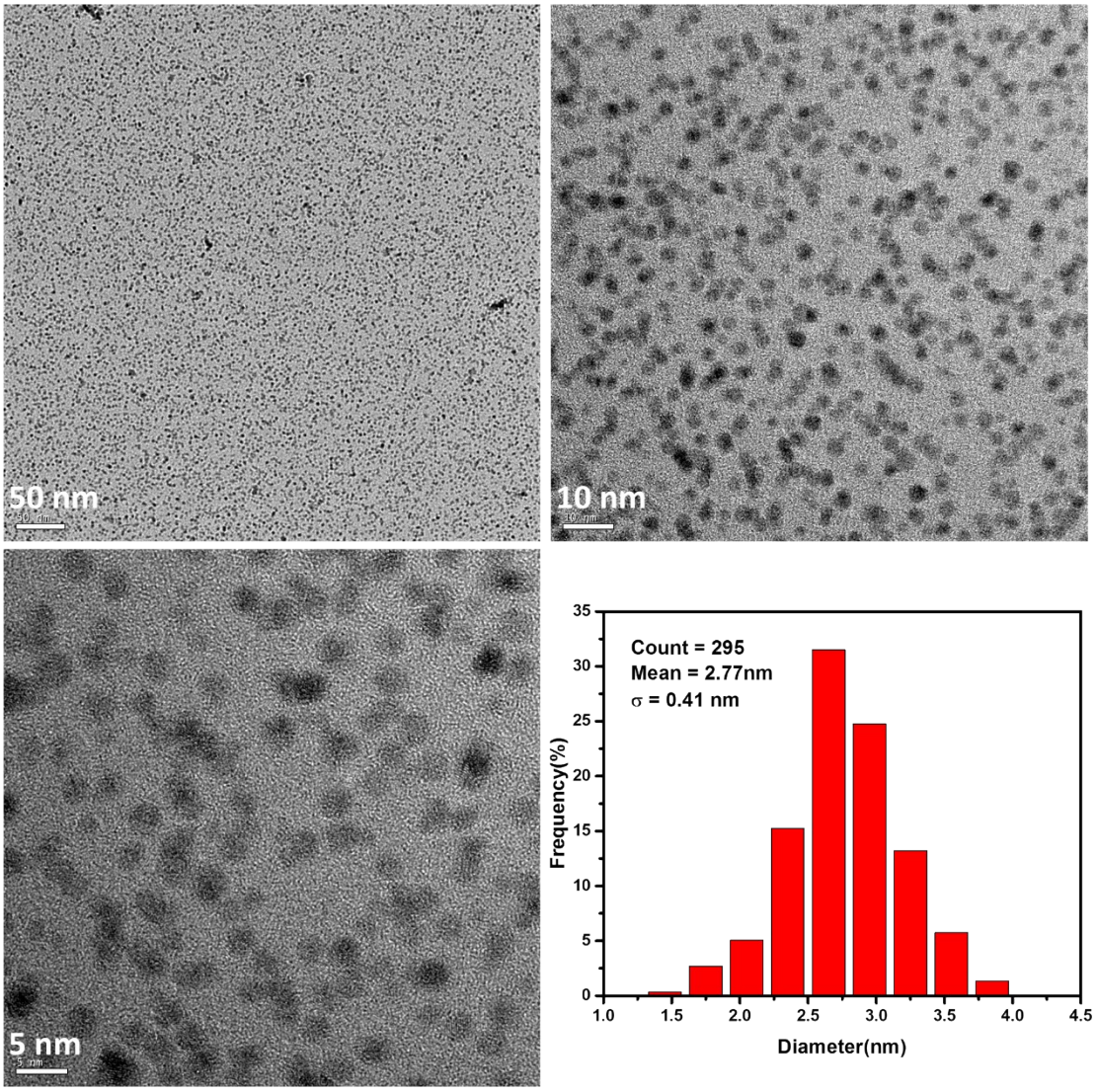

Fig. S1 The TEM image of Pd colloid nanoparticles and the corresponding of particles size distribution.

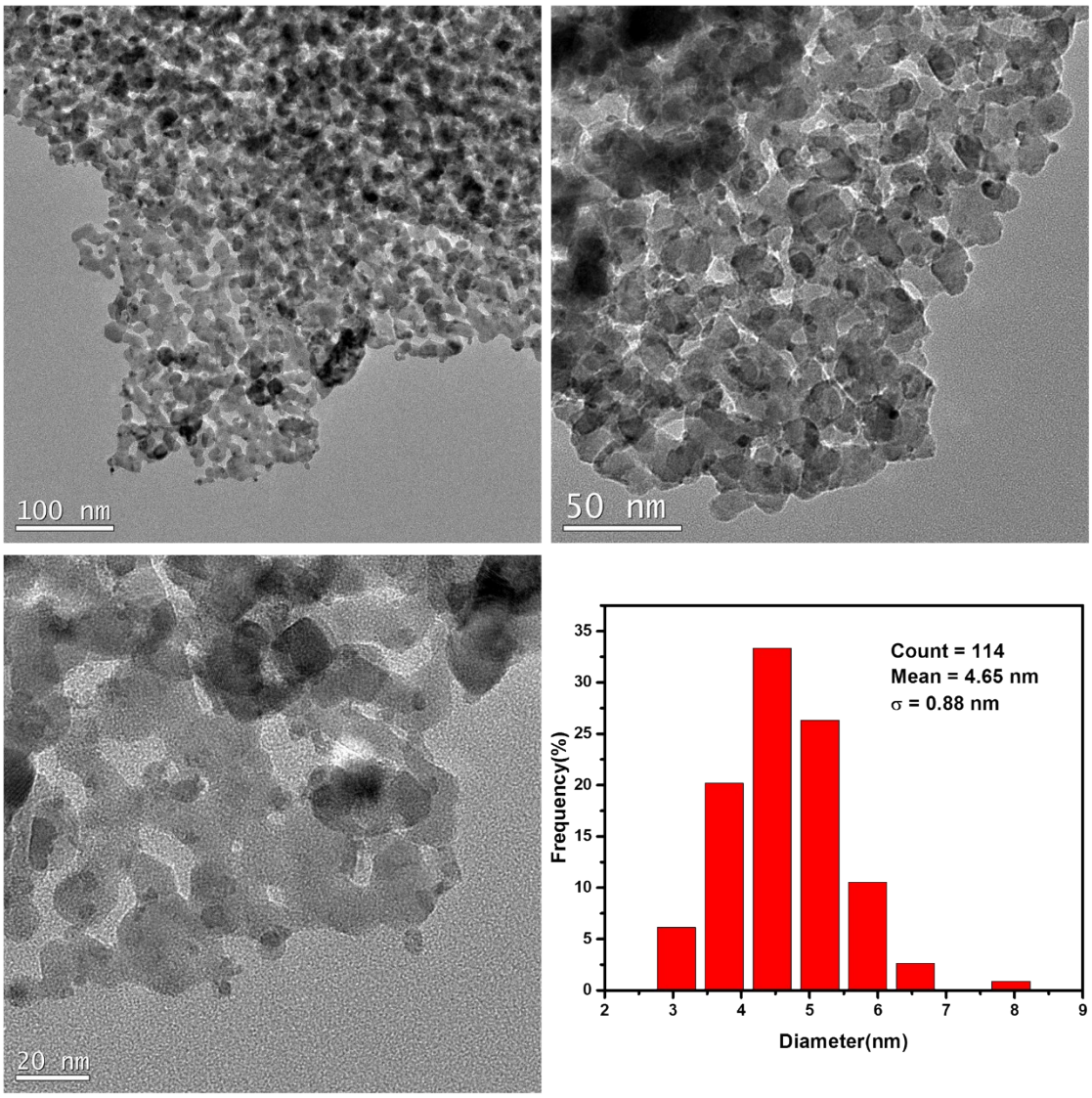

Fig. S2 The TEM image of WI-Pd/$NiCo_2O_4$ and the corresponding of Pd nanoparticles size distribution.

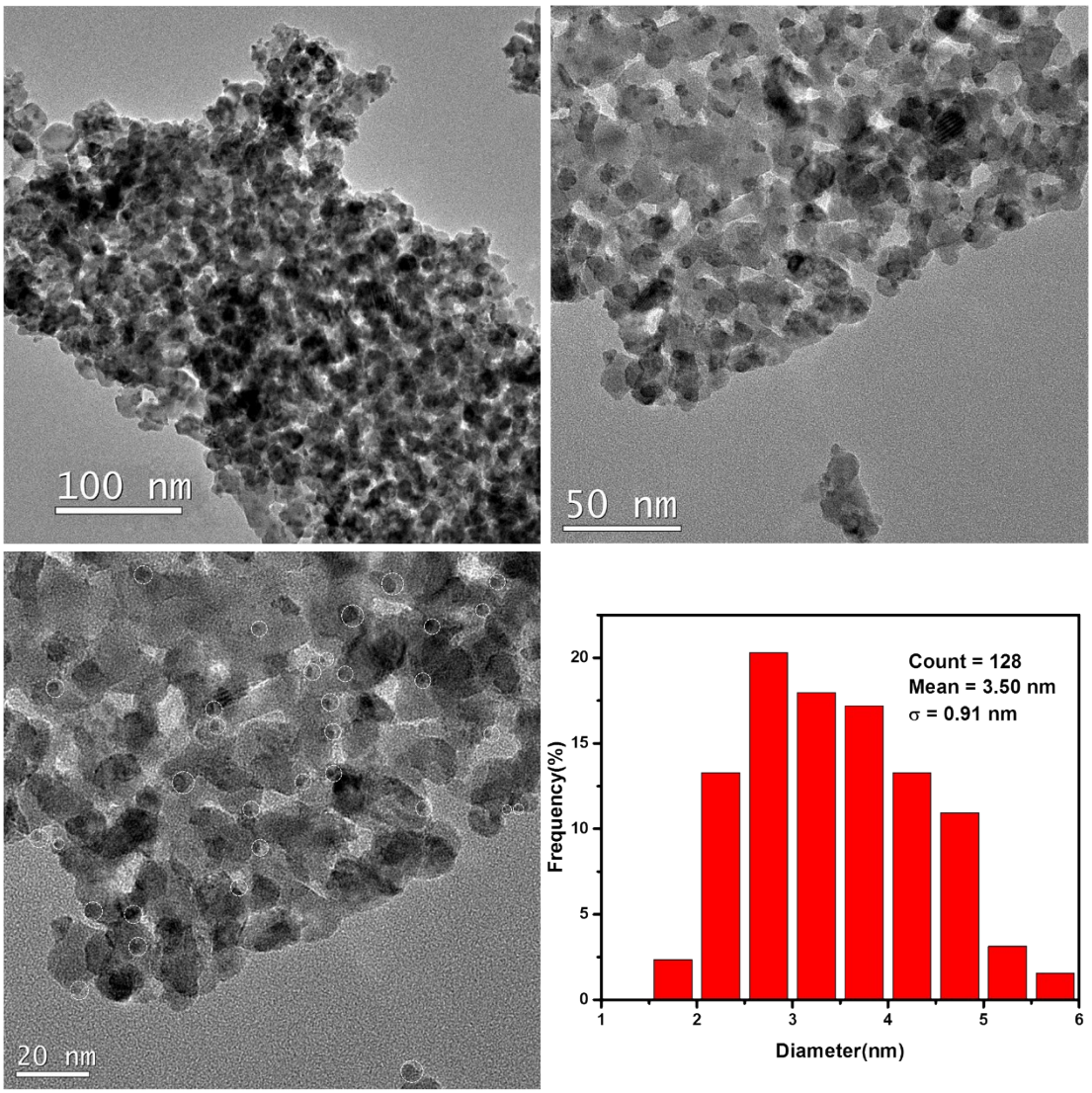

Fig. S3 The TEM image of Pd(3nm)/$NiCo_2O_4$ and the corresponding of Pd nanoparticles size distribution.

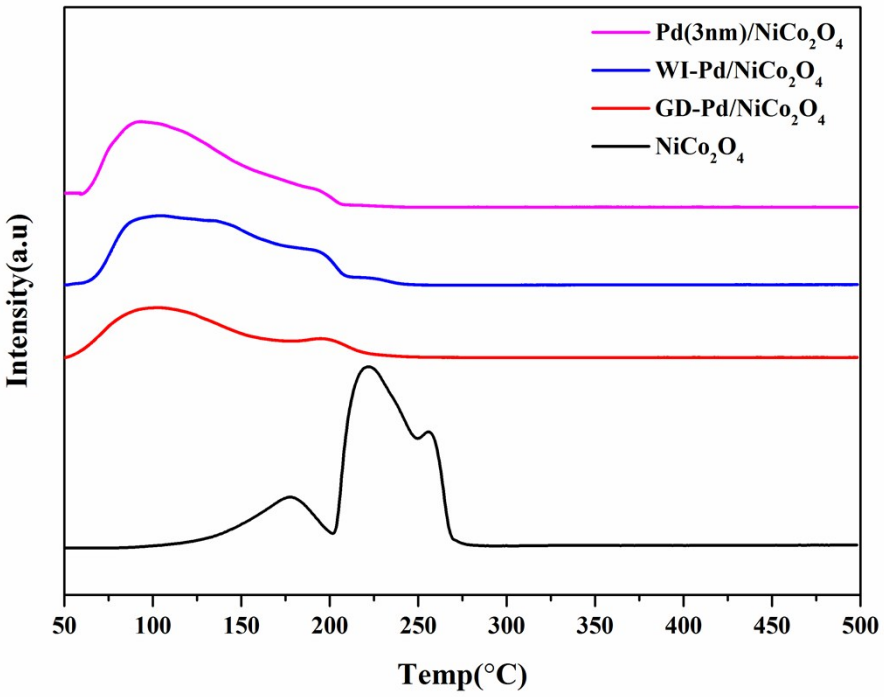

Fig. S4 H_2 –TPR profile of GD-Pd/$NiCo_2O_4$, Pd(3nm)/$NiCo_2O_4$, WI-Pd/$NiCo_2O_4$ and $NiCo_2O_4$.

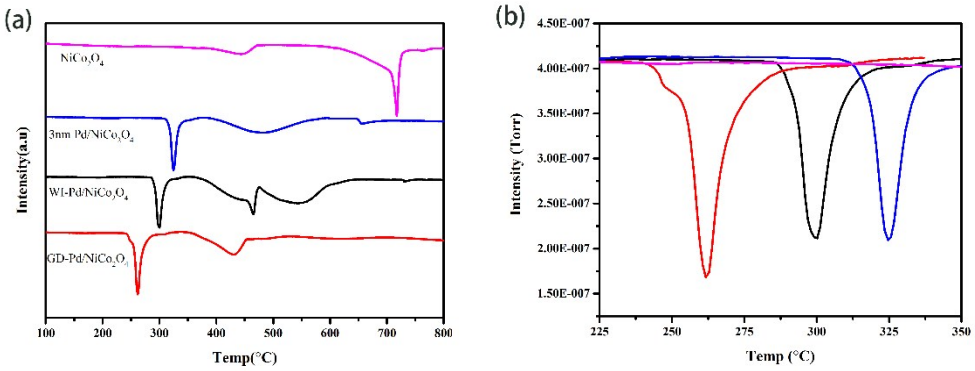

Fig. S5 CH_4-TPR results: the CH_4 signals of all samples.

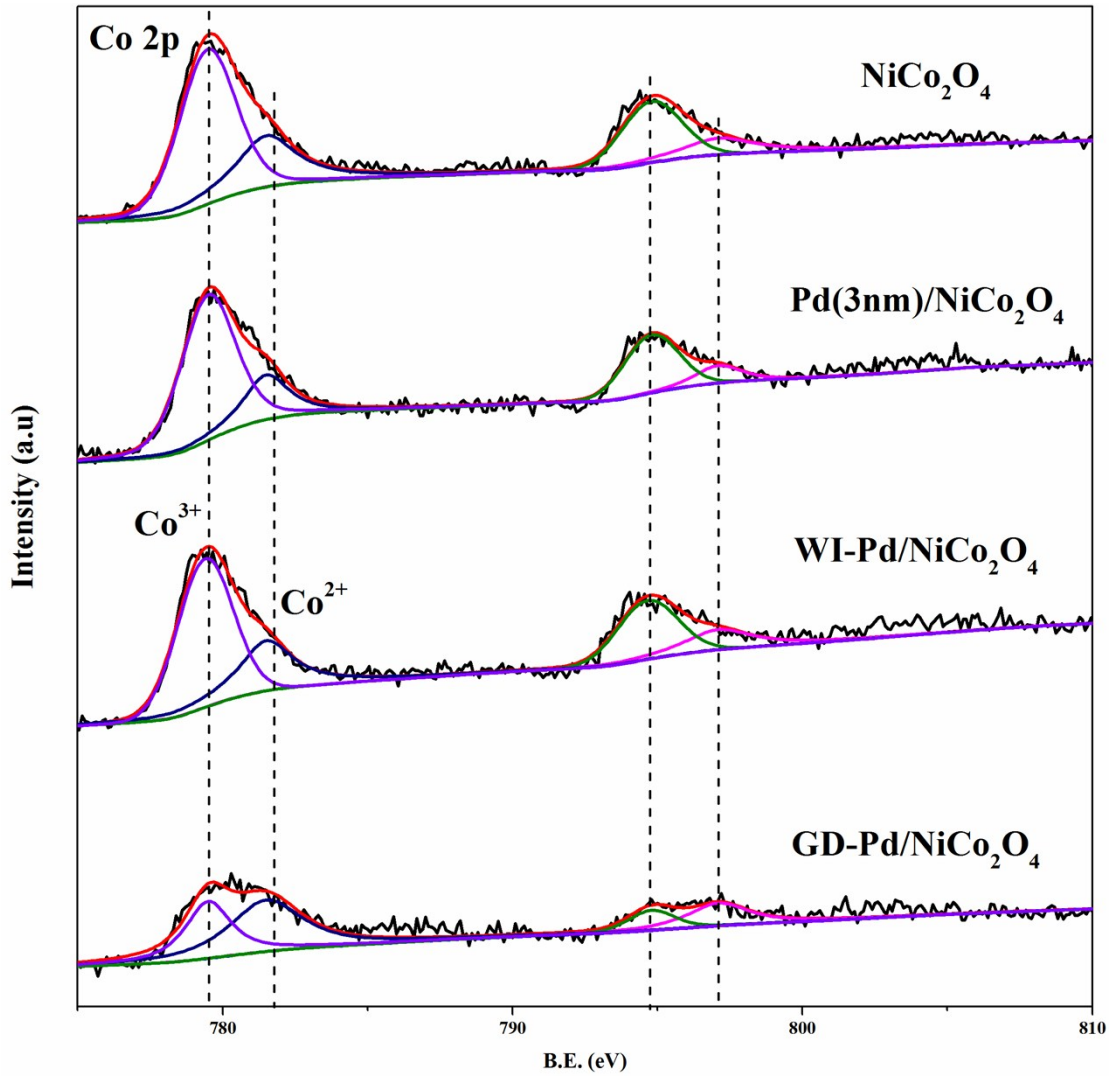

Fig. S6 Co *2p* XPS profiles of $NiCo_2O_4$, GD-Pd/$NiCo_2O_4$, WI-Pd/$NiCo_2O_4$ and Pd(3nm)/$NiCo_2O_4$.

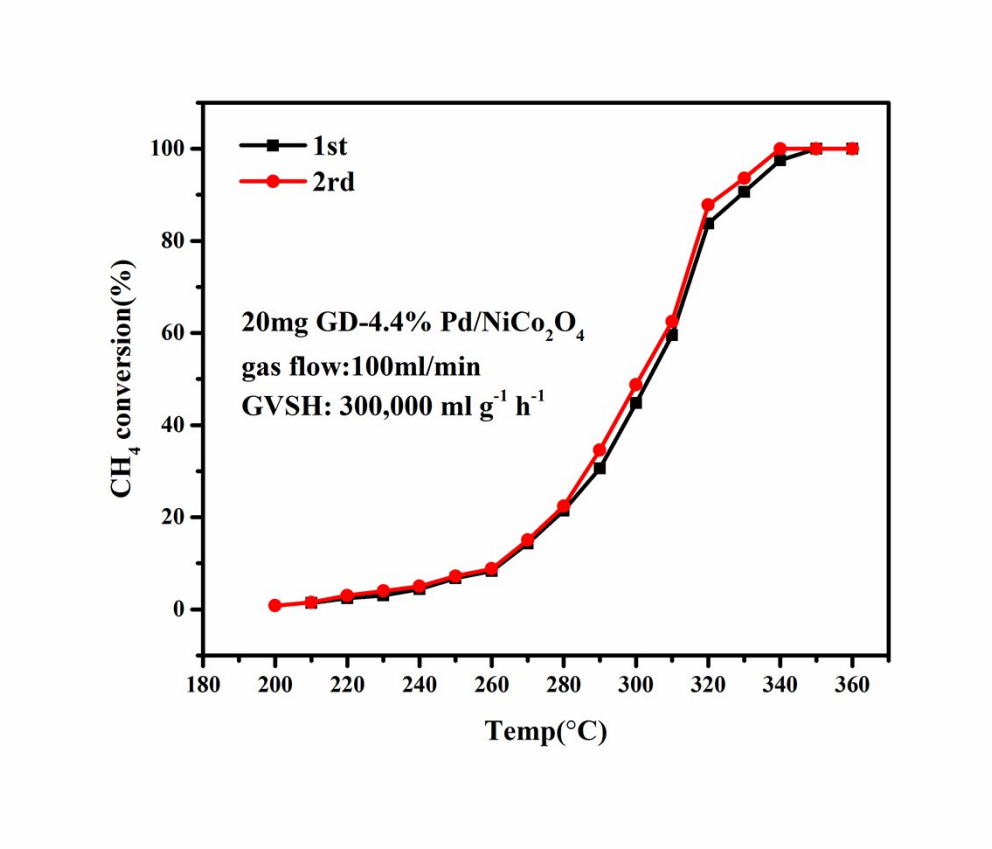

Fig. S7 Catalytic methane combustion performance of GD-Pd/$NiCo_2O_4$ at high GVSH. In this figure, the total oxidation of methane at temperature lower than 350 °C with only about 20mg catalytic material usage.

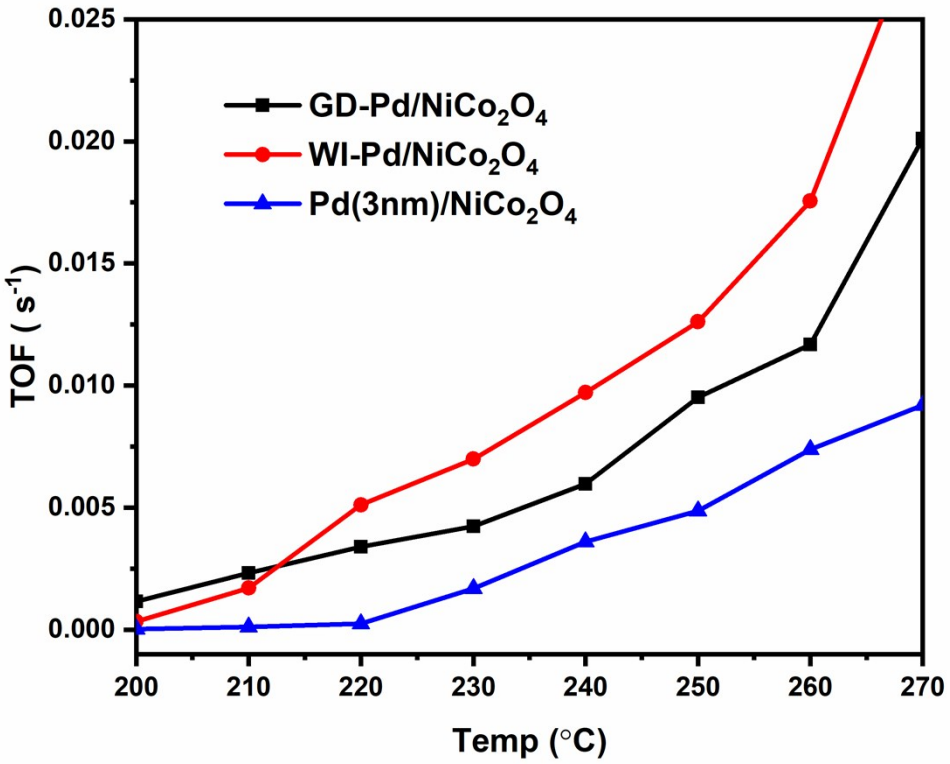

Fig. S8 Turnover frequency of $NiCo_2O_4$, GD-Pd/$NiCo_2O_4$, WI-Pd/$NiCo_2O_4$ and Pd(3nm)/$NiCo_2O_4$.

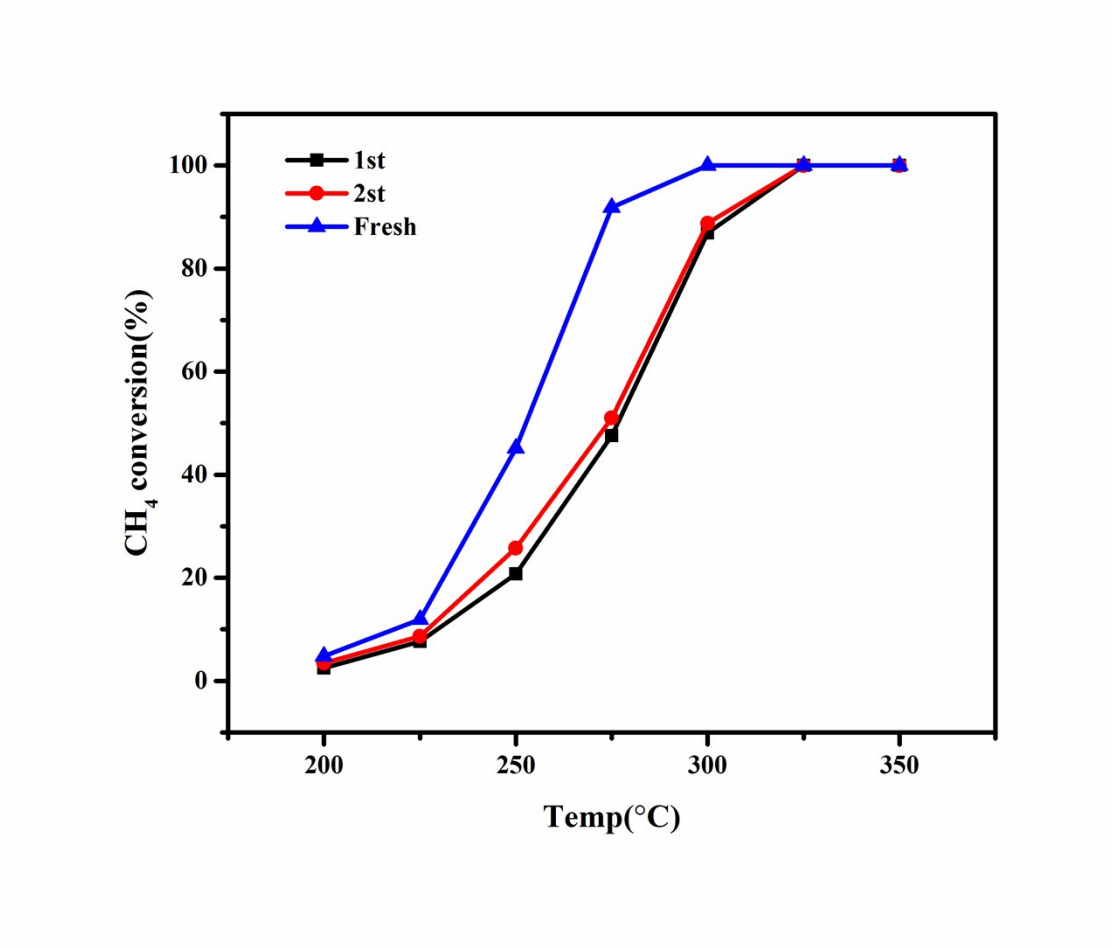

Fig. S9 GD-Pd/$NiCo_2O_4$ was revaluated the catalytic activity after water vapor for 25 h. Reaction condition: 1 vol.% CH_4/Air, GHSV = 60000 ml g^{-1} h^{-1}.

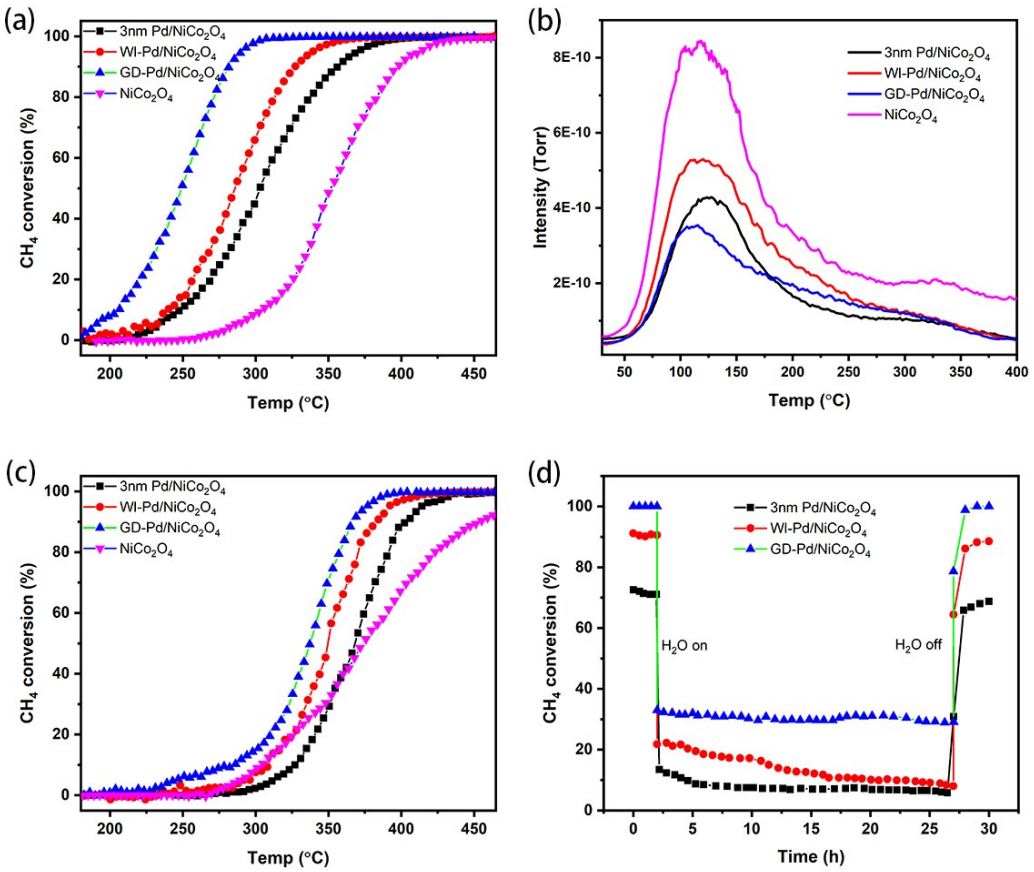

Fig. S10 (a) gas composition: 0.2% CH_4, 4% O_2 and 15% CO_2 balanced with Ar at GHSV = 60000 ml h^{-1} g^{-1}. (b) CO2-TPD. (c) gas composition: 0.2% CH_4, 4% O_2, 15% CO_2 and 10% H_2O balanced with Ar at GHSV = 60000 ml h^{-1} g^{-1}. (d) stability test of GD-Pd/$NiCo_2O_4$, WI-Pd/$NiCo_2O_4$ and Pd(3nm)/$NiCo_2O_4$ under the gas composition: 0.2% CH_4, 4% O_2 and 15% CO_2 and 10% H_2O balanced with Ar at GHSV = 60000 ml h^{-1} g^{-1}.

we evaluated the catalytic performance of our catalyst under operating conditions, which contained ultra-low concentrations of methane (about 0.2%) and large amounts of carbon dioxide (about 15%) and water vapor (about 10%). In **Fig. S10a**, the effect of CO_2 on the catalytic activity of the sample is limited. The GD-Pd/$NiCo_2O_4$ still has best catalytic performance with the T_{90} about 275 °C, which can be attributed to the fact that CO_2 readily desorbed from the catalyst surface above 200 °C (**Fig. S10b**). When the 10% water vapor was introduced into the reaction system, all of the catalysts decreased the catalytic performance. As shown in **Fig. S10c**, under the actual working conditions, only the GD-Pd/$NiCo_2O_4$ catalyst can achieve totally conversion of methane below 400 °C. Furthermore, GD-Pd/$NiCo_2O_4$ also displays long-term stability without significant decrease in activity. However, the conversion of CH_4 over WI-Pd/$NiCo_2O_4$ declines from 20% to 8% after 20 hours. Under the same condition, the methane conversion over Pd(3nm)/$NiCo_2O_4$ decreases from 12 to 5%.

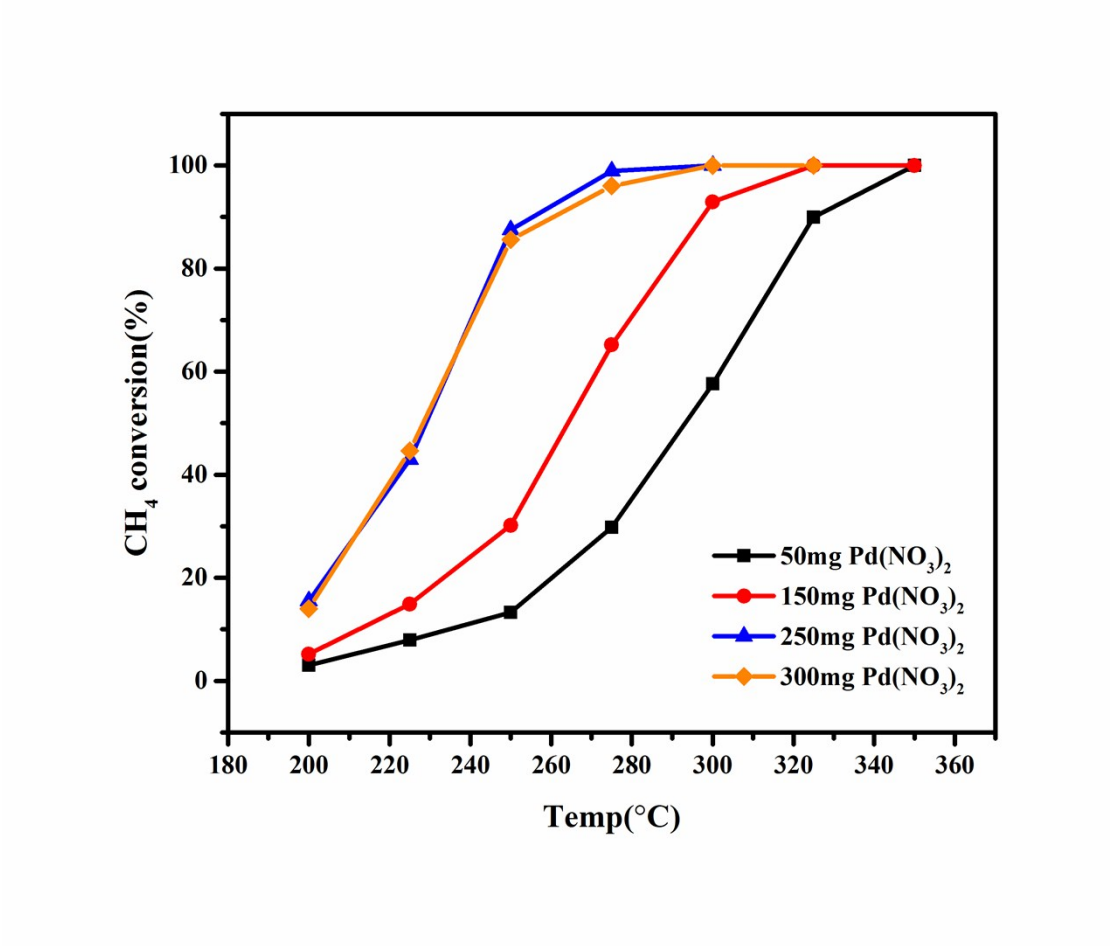

Fig. S11 Different concentration of Pd^{2+} ion added into the reaction system showing different catalytic activity. In this figure, the 250mg $Pd(NO_2)_3$ sample (4.4% GD-Pd/$NiCo_2O_4$) shows best catalytic performance at GHSV = 24000 ml h^{-1} g^{-1}.

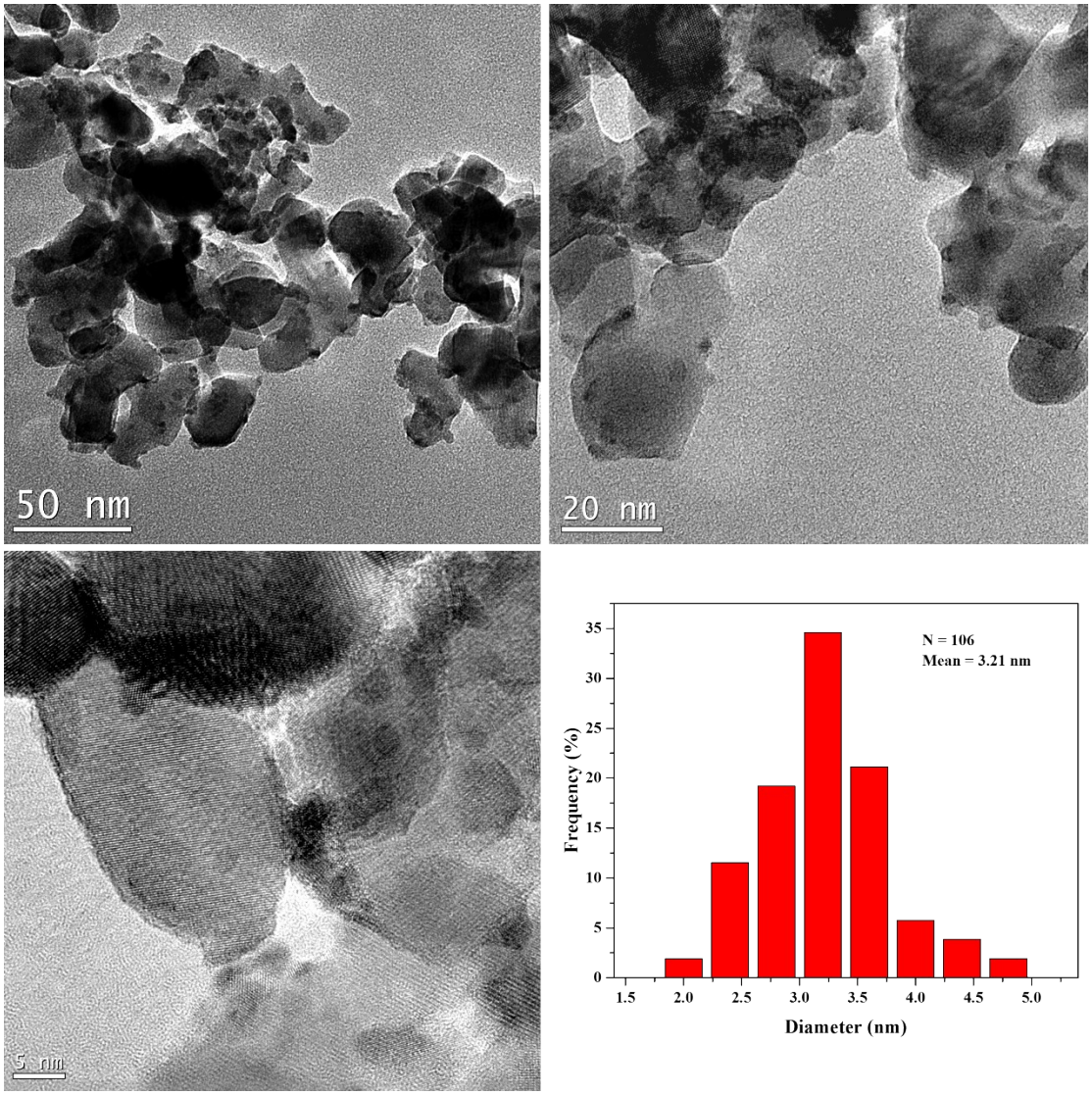

Fig. S12 The TEM and the HRTEM image of GD-Pd/Co_3O_4 sample.

References

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