## Plasmon-Driven Methanol Oxidation on PtAg Nanoalloys Prepared by

## **Improved Pulsed Laser Deposition**

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## **Supporting Information**



**Figure S1.** Morphology characterization of as-prepared samples. SEM images of Pt NP (a),  $Pt_{75}Ag_{25}$  NP (b),  $Pt_{50}Ag_{50}$  NP (c),  $Pt_{25}Ag_{75}$  NP (d), and Ag NP (e).



Figure S 2(a) Bright-field TEM images of  $Pt_{50}Ag_{50}$  nanoparticles. (b) TEM images of  $Pt_{50}Ag_{50}$  nanoparticles.



**Figure S 3** (a) STEM images of  $Pt_{50}Ag_{50}$  NP. (b) HAADF-STEM image of  $Pt_{50}Ag_{50}$  NP. (c) STEM images of  $Pt_{25}Ag_{75}$  NP. (d) HAADF-STEM image of  $Pt_{25}Ag_{75}$  NP.



**Figure S 4** Particle size distribution of as-prepared samples corresponding to Fig-S3. (a)  $Pt_{50}Ag_{50} NP$ , (b)  $Pt_{25}Ag_{75} NP$ .



**Figure S 5**(a, b) Plot of the binding energy of Pt 4f  $_{7/2}$  and Ag  $3d_{5/2}$  versus the Ag mole fraction in the precursor, respectively.



**Figure S 6** Cyclic voltammetry (CV) profiles of as-prepared samples in 0.1 M HClO<sub>4</sub> solution at a scan rate of 50 mV s<sup>-1</sup>. (a) Pt NP s, (b)  $Pt_{75}Ag_{25}$  NP. (c)  $Pt_{50}Ag_{50}$  NP, (d)  $Pt_{25}Ag_{75}$  NP.



Figure S 7 Cyclic voltammetry(CV) profiles of Ag NP in 0.1 M HClO<sub>4</sub> solution at a scan rate of 50 mV s<sup>-1</sup>.



**Figure S 8**(a, b) Cyclic voltammetry profiles of Pt and  $Pt_{75}Ag_{25}$  nanoparticles in 1 M KOH solution. (c, d) Cyclic voltammetry profiles during methanol oxidation reaction for Pt and  $Pt_{75}Ag_{25}$  nanoparticles in 1 M methanol and 1 M KOH solution. All graphs are at a scan rate of 50 mV s<sup>-1</sup>.



**Figure S 9** Cyclic voltammetry (CV) profiles of Ag NP in 1 M KOH solution (black) and in 1 M methanol + 1 M KOH solution (red) at a scan rate of 50 mV s<sup>-1</sup>.



**Figure S 10** Cyclic voltammetry profiles of as-prepared samples in 1 M KOH solution at a scan rate of 50 mV s<sup>-1</sup>. (a) Pt NP, (b) Pt<sub>75</sub>Ag<sub>25</sub> NP. (c) Pt<sub>50</sub>Ag<sub>50</sub> NP, (d) Pt<sub>25</sub>Ag<sub>75</sub> NP.



**Figure S11** Cyclic voltammetry profiles of methanol oxidation reaction(MOR) for  $Pt_{50}Ag_{50}$  NP 1 M KOH solution containing methanol of various concentrations at a scan rate of 50 mV s<sup>-1</sup>.



**Figure S12** Cyclic voltammetry profiles of methanol oxidation reaction (MOR) for  $Pt_{50}Ag_{50}$  NP with different substrate-target distance in 1 M methanol + 1 M KOH solution at a scan rate of 50 mV s<sup>-1</sup>.



**Figure S13** Cyclic voltammetry profiles of methanol oxidation reaction (MOR) for  $Pt_{50}Ag_{50}NP$  with different deposition time in 1 M methanol + 1 M KOH solution at a scan rate of 50mV s<sup>-1</sup>.



Figure S14 Diffuse reflectance UV-vis absorption spectroscopy of Pt, Pt<sub>75</sub>Ag<sub>25</sub>, Pt<sub>50</sub>Ag<sub>50</sub> and Pt<sub>25</sub>Ag<sub>75</sub> NP.



**Figure S15** Effect of the natural light on methanol oxidation reaction of  $Pt_{50}Ag_{50}$  NP in 1 M methanol + 1 M KOH solution at a scan rate of 50 mV s<sup>-1</sup>.



**Figure S16** Effect of the UV light of 640 nm and 468 nm on methanol oxidation reaction of  $Pt_{50}Ag_{50}$  NP in 1 M methanol + 1 M KOH solution at a scan rate of 50 mV s<sup>-1</sup>.

Table S1. T	he elemental	compositions	obtained by	y EDX and	XPS and	alysis for	three d	lifferent l	PtAg (	catalysts
synthesized	l by PLD.									

	EDV analys	ic [ a+9/ ]	XPS analysis [at%]			
Catalyst	EDX analys	IS [at%]				
	Ag	Pt	Ag	Pt		
$Pt_{75}Ag_{25}$	23.16	76.84	24.78	75.22		
$Pt_{50}Ag_{50}$	51.55	48.45	53.79	46.21		
$Pt_{25}Ag_{75}$	76.41	23.59	79.87	20.13		

Catalyst	Electrolyte concentrati	Methanol concentrati	Scan rate	Current density	I <sub>f</sub> /I <sub>b</sub>	Ref.
Pt NP	1	1	50	0.89	6.4	This work
Pt <sub>75</sub> Ag <sub>25</sub> NP	1	1	50	1.7	9.5	This work
Pt <sub>50</sub> Ag <sub>50</sub> NP	1	1	50	3.6	20.7	This work
Pt <sub>25</sub> Ag <sub>75</sub> NP	1	1	50	2.97	7.4	This work
PtC	0.2	1	50	0.351	7.4	1
AgAu@Pt	0.2	1	50	0.4831	34.3	1
Pt-Ag/C	1	1	50	4.3482	5.65	2
Pt-Ag/G	1	1	50	5.6283	_	2
Pt-Ag/C	0.5	0.5	50	_	10.67	3
Pt-Bi/GNs	1	1	50	2	_	4
p-Pt <sub>1</sub> Cu <sub>1</sub> /AP-	0.1	0.5	50	3.61	10.44	5
GNP						
PdPt/CNTs	0.5	0.5	50	1.10	4.23	6
Pt/G₃DN	1	1	50	0.91	3.08	7
Pt/P-Ni	1	0.5	100	1.38	—	8
$Pd_1Pt_1NWs$	0.5	0.5	50	_	1.83	9
Graphene-Pt NP	0.1	0.5	10	1.18	4.03	10
hybrid						
$Au_1Pt_3$	0.5	0.5	50	0.1335	—	11
Co₃Pt	1	1	50	_	12.1	12
Pt/carst-Ni	1	1	20	_	6.25	13
Fe <sub>3</sub> O <sub>4</sub> @CeO <sub>2</sub> /Pt- 20%	0.5	1	50	0.273	4.5	14
PtAuRu/RGO/GC	1	1	50	1.6505	_	15
PtCu NFs	0.5	1	50	2.26	2.7	16
Pd@Pt/RGO	0.5	0.5	50	4.972	_	17

**Table S2.** Performance parameters in terms of mass activity, ratio of forward/backward anodic peak current density  $(I_f/I_b)$ .

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