

One-Pot Synthesis of Surfactant-Free Core@Shell PdAuPt Nanodendrites@Pd Nanosheets for Boosted Visible Light Driven Methanol Electrooxidation

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1. Experimental section

Materials and chemicals: Palladium acetate ($\text{Pd}(\text{OAc})_2$, 98%), Tungsten carbonyl ($\text{W}(\text{CO})_6$, 97%), Chloroauric acid tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, A.R. grade, 99%), and Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 99%) came from Shanghai Macklin Co. Ltd. N, N-Dimethylformamide (DMF, >99.5%), Acetic acid (AA, 99%). Methanol (CH_3OH , AR grade, 99.9%), and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, AR grade, 99.7%) were from Sinopharm Chemical Reagent Co. Ltd., Water (H_2O , 18 $\text{M}\Omega/\text{cm}$) used in tests was prepared through flowing through an ultra-pure purification system.

Preparation of PdPtAu@Pd core@shell Catalysts: In a preparation of PdPtAu@Pd catalysts, 10 mg of $\text{Pd}(\text{OAc})_2$, 1.6 mg of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, 2.0 mg $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 30 mg of $\text{W}(\text{CO})_6$, 2 mL acetic acid were added in a vial containing 8 mL DMF in sequence. The precursor compound was mixed and dissolved fully under ultrasonication. Afterwards, the vial was removed to an oil bath and heated up to 140 °C for 60 min. After cooling down to room temperature, the final products were denoted as PdPtAu@Pd catalysts, and collected by centrifugating and washing with the ethanol solution for several times.

Characterizations: The structure characterizations of the obtained products were firstly conducted by transmission electron microscope (TEM, accelerating voltage: 120 kV, HT-7700) and high resolution TEM (HRTEM, operation voltage: 200 kV, F20). The phase structure was investigated by X-ray diffraction (XRD) spectra recorded on a X'Pert-Pro MPD diffractometer (Netherlands PANalytical) operating at 40 kV with Cu K α radiation. The elemental composition and chemical states of the sample were analyzed by scanning electron microscope energy-dispersive X-ray spectroscopy (SEM-EDS, working voltage: 15 kV) and X-ray photoelectron spectroscopy (XPS) that conducted on a VG Scientific ESCALab 220 XL electron spectrometer with 300 W Al K α radiation, respectively.

Electrochemical measurements: The electrochemical tests were performed on an Electrochemical Work Station (CHI660E Shanghai Chenhua Instrument Corporation, China) with a three-electrode electrochemical cell including the working electrode (glassy carbon electrode, GCE, diameter: 3 mm), the counter electrode (platinum wire), and the reference electrode (KCL saturated calomel electrode, SCE). The calibration technique was also adopted to ensure the stability of reference electrode.^[60] The obtained catalysts were dispersed in a mixture containing isopropanol and Nafion (5%) to form a 0.40 mg_{metal}/mL dispersion. Subsequently, 5 μ L catalytic ink was deposited on a GCE and dried naturally to fabricate the catalyst-coated working electrode. MOR measurements were conducted in 0.5 M KOH + 1 M methanol solution. In addition, a 150 W power xenon lamp with UV cut-off filter (> 400 nm) was applied to supply visible light.

2. Supporting figures and tables

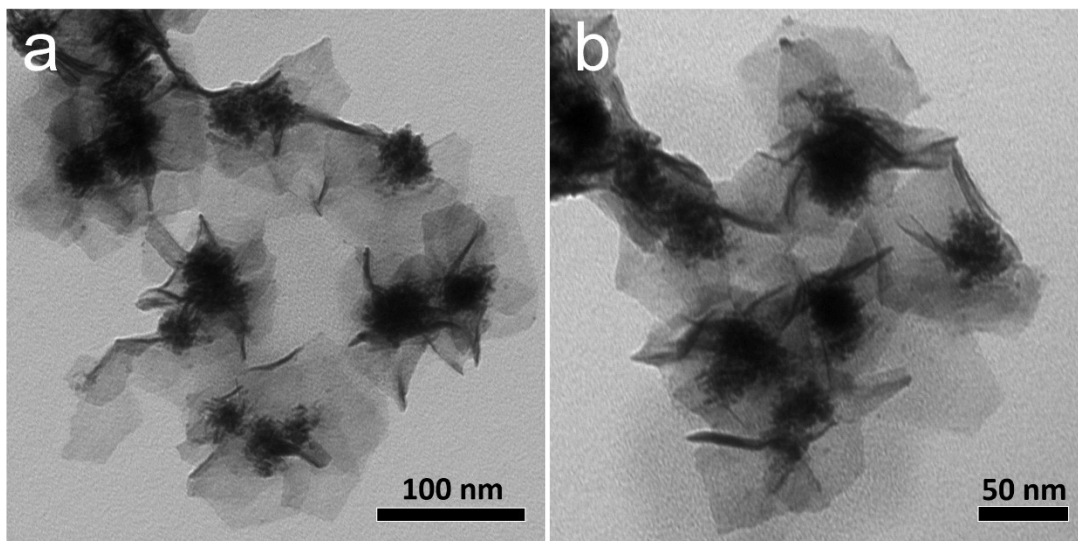


Figure. S1 Additional TEM images of PdPtAu@Pd core@shell nanocatalysts.

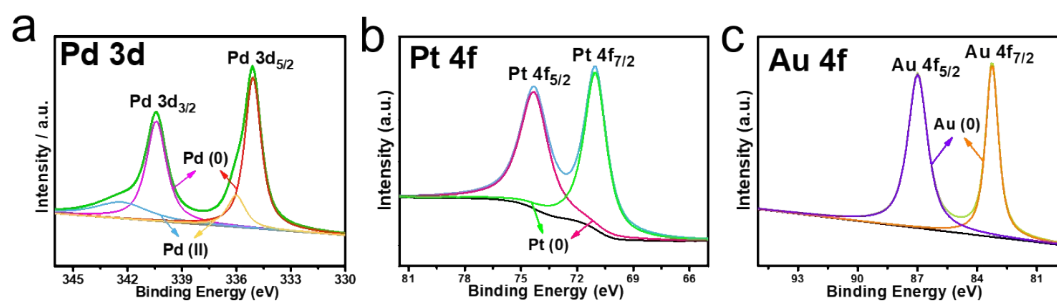


Figure. S2 XPS spectra of (a) Pd 3d, and (b) Pt 4f, and (c) Au 4f in PdPtAu@Pd core@shell nanocatalysts.

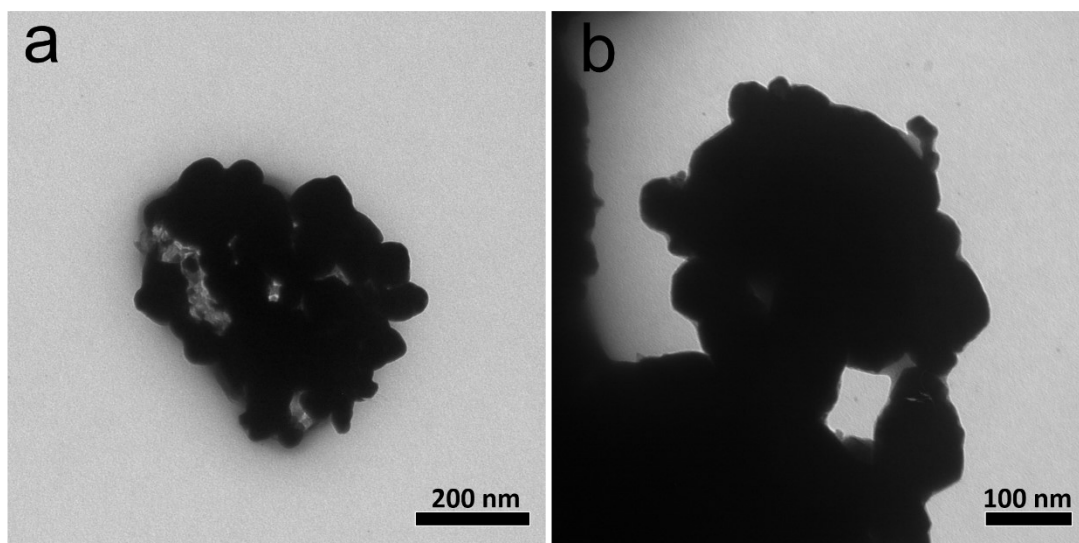


Figure. S3 (a and b) TEM images of the products with the same reaction conditions as that of PdPtAu@Pd without the addition of $W(CO)_6$.

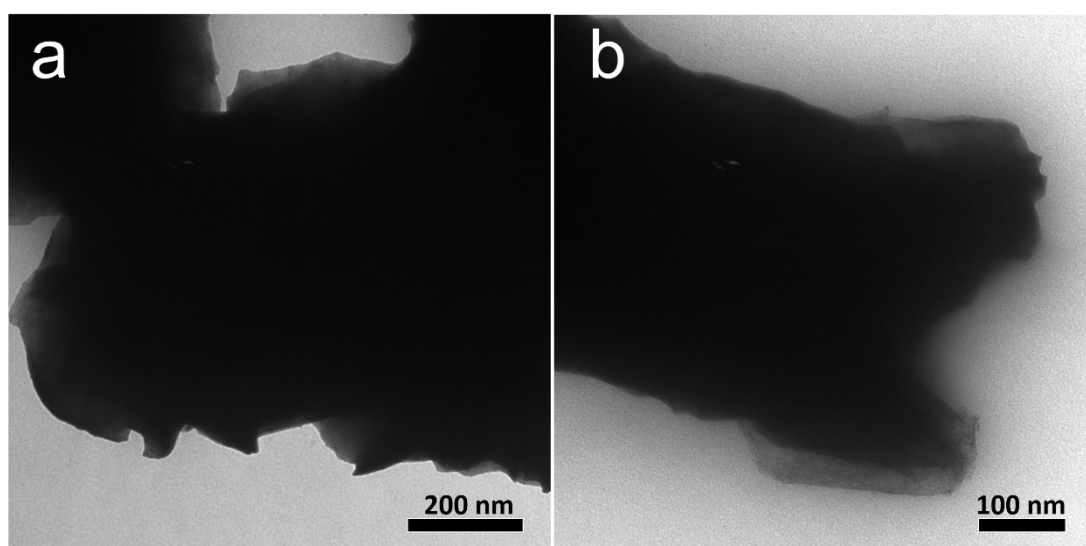


Figure. S4 (a and b) TEM images of the products with the same reaction conditions as that of PdPtAu@Pd without the addition of AA.

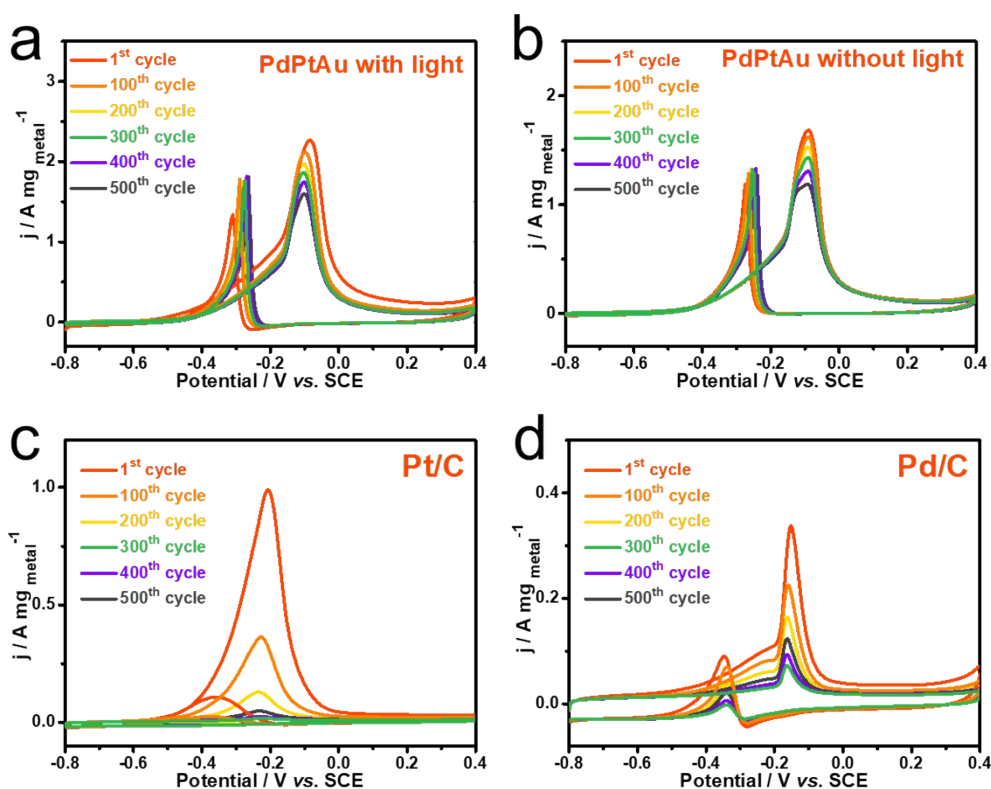


Figure. S5 CV (1st, 100th, 200th, 300th, 400th and 500th) curves of (a) PdPtAu@Pd with light, (b) PdPtAu@Pd without light, (c) Pt/C, and (d) Pd/C catalysts recorded in 0.5 M KOH + 1 M methanol solution.

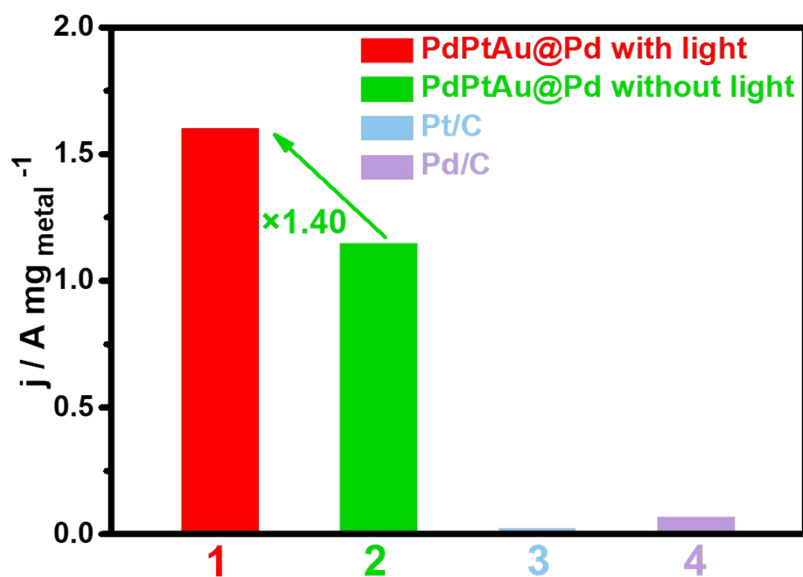


Figure. S6 Retained mass activities of the tested catalysts after consecutive CV tests for MOR.

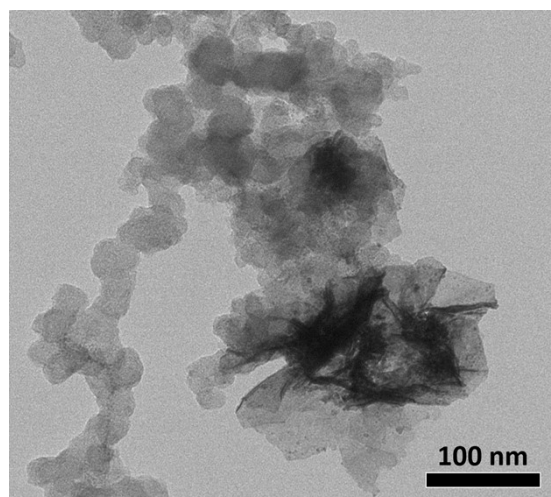


Figure. S7 TEM images of PdPtAu@Pd core@shell catalysts after 500 CV cycles.

Table S1. MOR performances of PdPtAu@Pd core@shell catalysts and various electrocatalysts from published works.

Catalysts	Peak currents from CV curves	Electrolyte	Reference
	J_m (A mg ⁻¹)		
PdPtAu@Pd	2.266	0.5 M KOH + 1 M methanol	This work
Pd ₄ Sn WNWs	1.04	0.1 M KOH + 0.5M methanol	<i>Nano Lett.</i> 2019 , 19, 6894–6903
Pd-PdO PNTs	1.11	0.1 M KOH + 0.3 M methanol	<i>Adv. Funct. Mater.</i> 2020 , 30, 2000534.
Pd ₇₂ Cu ₁₄ Co ₁₄	1.062	1 M KOH + 1 M methanol	<i>Energy Chem.</i> 2019, 29 , 72.
PdCo	1.08	1 M KOH + 1 M methanol	<i>ACS Appl. Mater. Interfaces</i> 2018 , 10, 29965
PdAg@Pd	0.69	0.5 M NaOH + 0.5 M methanol	<i>J. Power Sources</i> 2018 , 398, 201.
PdAuCu	1.046	1 M KOH + 1 M methanol	<i>Electrochim. Acta.</i> 2017 , 227, 330
Pd ₂ Cu ₂	0.916	1 M KOH + 1 M methanol	<i>J. Mater. Sci.</i> 2018 , 53, 15871.
Pd _{0.52} Ag	0.72	0.5 M NaOH + 1 M methanol	<i>Angew. Chem., Int. Ed.</i> 2019 , 58, 8794

3. MOR pathway mechanism

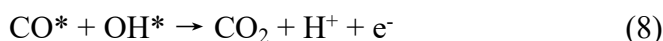
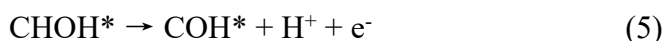
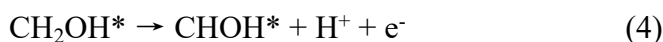
The MOR pathway could be explained by the following equations. Generally, the methanol electrooxidation is a slow kinetic process with 6e⁻ transfer, including the absorption, dehydrogenation, and oxidation process, which could be illustrated in the following equations [1-3].

6e⁻ pathway mechanism:

i) absorption process:



ii) dehydrogenation process:



As illustrated in the elementary reactions, the methanol molecule firstly absorbed on the surfaces of catalysts to form the $\text{CH}_3\text{OH}_{\text{ads}}$ species (equation (1)), and then dehydrogenated and decomposed to form carbon intermediate species CO^* , the CO species could be gradually dehydrogenated by CH_2OH^* , CHOH^* , COH^* (equation (2-6)). In alkaline media, the MOR mechanism went through two possible pathways. However, the CO^* could combine with OH^- to form the OH^* in alkaline conditions, thus to form the ultima CO_2 products.

References

- 1 H. Meng, Y. Zhan, D. Zeng, X. Zhang, G. Zhang, F. Jaouen, *Small*, 2015, 11, 3377-3386.
- 2 Y. Xu, B. Zhang, *Chem. Soc. Rev.* 2014, 43, 2439-2450.
- 3 N. Kakati, J. Maiti, S.H. Lee, S.H. Jee, B. Viswanathan, Y.S. Yoon, *Chem. Rev.* 2014, 114, 12397-12429.