

Supporting Information

for

Assembling Palladium and Cuprous Oxide Nanoclusters into Single Quantum Dots for Electrocatalytic Oxidation of Formaldehyde, Ethanol, and Glucose

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1. Experimental

Materials characterization

X-ray diffraction (XRD) diffractograms were measured with a Miniflex II diffractometer equipped with CuK α radiation, where the X-ray tube operated at 30 kV with a current of 5 mA. X-ray photoelectron spectroscopy (XPS) spectra were acquired using a Scienta Omicron HiPP-3 analyzer and a monochromatic Al K α source operating at 20mA emission current. The base pressure was about $2 \cdot 10^{-9}$ mbar, and the operating pressure was about $5 \cdot 10^{-9}$ mbar. Survey and high-resolution spectra were acquired at pass energies of 300eV and 100eV respectively. Data analysis and quantification were performed using KolXPD from Kolibri. The morphology and surface composition of both the fresh and the spent catalysts were characterized using the Talos F200S Field Emission Transmission Electron Microscope (TEM) equipped with an Energy Dispersive X-ray Spectrometer (EDS). The accelerating voltage was 200 kV. For the electrochemical experiments a Gamry reference 600 potentiostat and Gamry eQCM 10M were used.

Procedure for the preparation of Cu/C material

Vulcan VXC-72R (500 mg) was activated under vacuum at 120 °C for 18 hours. Then it was impregnated under vacuum with a Cu(NO₃)₂·3H₂O solution (152 mg in 0.2 mL DI water) under vigorous stirring. Afterwards, the Cu(NO₃)₂/C material was dried at 100 °C for 18 hours and reduced at 250 °C for 1 h in a 5% H₂/N₂ atmosphere (Ramp 5 °Cmin⁻¹, flowrate 150 mLmin⁻¹).

General procedure for the preparation of Pd-Cu/C QDA

A palladium solution (Pd(NO₃)₂·xH₂O Pd \geq 39% in 50 mL DI water, amounts varies per material) was degassed with nitrogen for >30 minutes, to which 200 mg Cu/C material was directly added, limiting the exposure time to O₂. The suspension was sonicated for 30 min and agitated for 18 hours to complete the galvanic replacement of Cu by Pd. The Pd-Cu/C was filtered, washed with 100 mL DI water and dried under vacuum at room temperature.

Example ₂Pd-₈Cu/C

A palladium solution (Pd(NO₃)₂·xH₂O Pd \geq 39%, 10.3 mg in 50 mL DI water) was degassed with nitrogen for >30 minutes, to which 200 mg Cu/C material was directly added, limiting the exposure time to O₂. The suspension was sonicated for 30 min and agitated for 18 hours to complete the

galvanic replacement of Cu by Pd. The $\text{Pd}_8\text{Cu}/\text{C}$ was filtered, washed with 100 mL DI water and dried under vacuum at room temperature.

General procedure for the preparation of Pd/C control samples

Vulcan VXC-72R (500 mg) was activated under vacuum at 120 °C for 18 hours. Then it was impregnated under vacuum with a $\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ solution ($\text{Pd} \geq 39\%$, varying mg in 0.2 mL DI water) under vigorous stirring. Afterwards, the $\text{Pd}(\text{NO}_3)_2/\text{C}$ material was dried at 100 °C for 18 hours and reduced at 160 °C for 1 h in a 5% H_2/N_2 atmosphere (Ramp 5 °Cmin⁻¹, flowrate 150 mLmin⁻¹).

Example Pd/C

Vulcan VXC-72R (500 mg) was activated under vacuum at 120 °C for 18 hours. Then it was impregnated under vacuum with a $\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ solution ($\text{Pd} \geq 39\%$, 10.2 mg in 0.2 mL DI water) under vigorous stirring. Afterwards, the $\text{Pd}(\text{NO}_3)_2/\text{C}$ material was dried at 100 °C for 18 hours and reduced at 160 °C for 1 h in a 5% H_2/N_2 atmosphere (Ramp 5 °Cmin⁻¹, flowrate 150 mLmin⁻¹).

Electrochemical procedures

Catalyst inks were prepared by suspending the catalysts (3 mg) in an ethanol:water mixture (2.1:0.9 mL) with 30 μL Nafion® (D-521 dispersion 5 wt.% in water/isopropanol) and sonicated for 18 hours.

Formaldehyde oxidation and ECD related reactions were measured in a standard three-electrode system was used with a glassy carbon working electrode (0.5 mm diameter) drop casted 3 times with 10 μL of catalyst ink and dried at 50 °C after each drop. A Saturated Calomel Electrode (SCE) and a Pt wire were used as the reference and counter electrodes, respectively. The bath-compositions are depicted in Table S2, and were purged with high purity nitrogen gas (99.999%) and maintained at 45 °C before the experiments. Cyclic voltammetry (CV) curves were recorded at 50 mVs⁻¹. For all experiments except copper reduction, CV or LSV curves were recorded till a stable signal was observed (for copper reduction this would change the electrode properties, because of copper plating).

For the eQCM experiments, catalysts were spray painted on a 5 MHz Au quartz crystal (Gamry) using an airbrush and catalyst ink prepared by suspending 1 mg catalyst in 1 mL ethanol.

The amount of loaded catalyst was determined by using the change in frequency of the quartz crystal before and after loading of the catalyst. The crystal with catalyst was loaded in a QCM flow cell (Gamry), were the catalyst functions as a working electrode. A platinum tube counter electrode and Ag/AgCl reference electrode. The electroless copper deposition was started by introducing the ECD-bath in the chamber. During the experiment a flow of 0.5mLmin⁻¹. The potential was measured using chronopotentiometry at a 0 mA current. The mass change was derived using the equation:

$$\Delta m = \frac{\Delta F A \sqrt{\mu \rho}}{-2F_0^2}$$

where ΔF is the frequency change of the quartz crystal, A is the active area of the quartz crystal, μ is the sheer modules, ρ is the density of quartz, F_0 is the fundamental frequency of the quartz crystal, and Δm is the mass gain.

Glucose and ethanol oxidation were measured in a in a standard three-electrode system was used with a glassy carbon working electrode (0.3 mm diameter) drop casted 9 times with 1 μ L of catalyst ink and dried at 50 °C after each drop. A Saturated Calomel Electrode (SCE) and a Pt wire were used as the reference and counter electrodes, respectively. Ethanol oxidation was recorded in a 1.0 M KOH + 1.0 M ethanol solution. Glucose oxidation was recorded in a 0.5 M KOH + 0.5 M glucose solution. Before the experiments, the electrolyte was purged with high purity nitrogen gas (99.999%) and maintained at 25 °C. The CV curves were recorded at 50 mVs⁻¹. CV curves were recorded till a stable signal was observed.

DFT simulations

The density-functional theory (DFT) calculations were performed, with the Vienna ab initio simulation package (VASP), using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional. The projector augmented wave (PAW) method was used to describe the electron-ion interaction. The 4 \times 4 Cu₂O (111) and Pd (111) slabs, each with three atomic layers with a vacuum spacing of at least 20 Å were constructed. The Pd₄₆ cluster with the (310) facet binding the Cu₂O surface were used to model the Pd-Cu₂O QDA. In all the calculations, an energy cutoff of 400 eV was used for the plane-wave expansion of the electronic wave function. The force and energy convergence criterion was set to 0.05 eV/Å and 10⁻⁴ eV, respectively.

2. Additional Figures

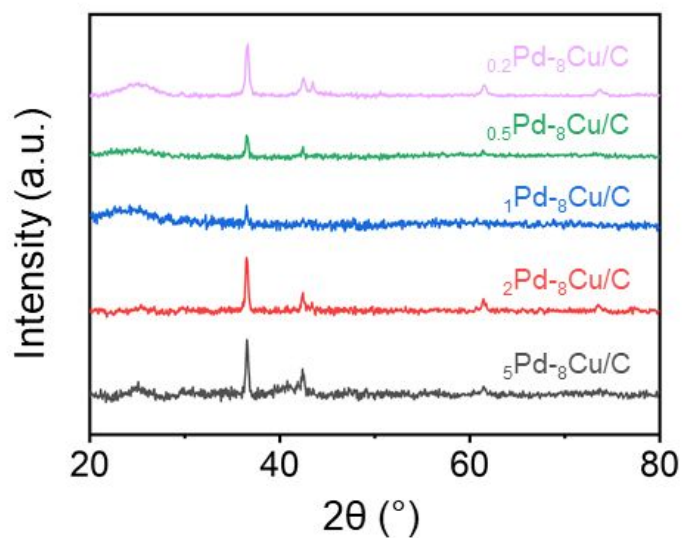


Figure S1. The XRD spectra of the Pd-Cu₂O QDAs with different palladium loadings.

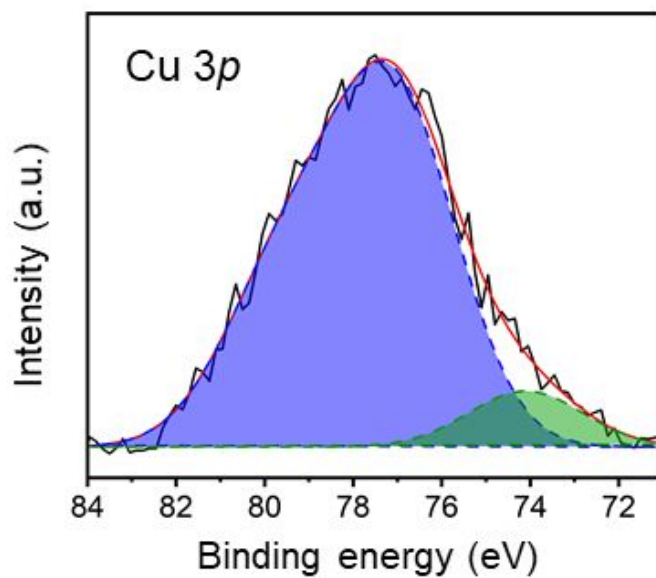


Figure S2. The Cu 3p XPS spectrum of the 5Pd-8Cu/C QDA.

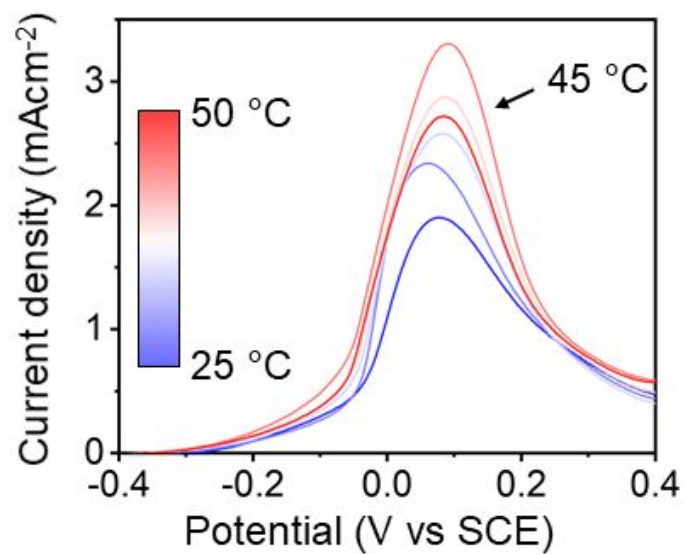


Figure S3. CV curves showing the dependency of the current density of formaldehyde oxidation on the temperature. The CVs are recorded in a copper-free ECD bath, saturated with N₂ and with a scan rate of 50 mVs⁻¹.

3. Additional Tables

Table S1. The fitting parameters for the XPS spectra and the derived data.^a

Main peak	Fitted peak	Binding energy	Lwid	Gwid	Peak area
Pd3d	Pd ⁰ 3d _{5/2}	335.80 eV	0.84	1.25	481
	PdO _x 3d _{5/2}	337.74 eV	0.84	0.84	3947
	Pd ⁰ 3d _{3/2}	341.12 eV	0.84	1.25	321
	PdO _x 3d _{3/2}	343.06 eV	0.84	1.23	2631
Cu2p	CuO 2p _{3/2} (1)	933.92 eV	0.14	2.37	3413
	CuO 2p _{3/2} (2)	935.29 eV	0.20	3.48	3523
	Cu ₂ O 2p _{3/2}	933.44 eV	0.56	3.23	297
	CuO 2p _{3/2} (1) sat.	942.46 eV	0.23	4.06	3082
	CuO 2p _{3/2} (2) sat.	944.51 eV	0.08	1.34	661
	CuO 2p _{3/2} (3) sat.	941.33 eV	0.23	4.06	330
	CuO 2p _{1/2}	953.92 eV	0	3.65	2818
	Cu ₂ O 2p _{1/2}	953.44 eV	0.56	3.23	149
	CuO 2p _{1/2} sat	962.65 eV	0	2.86	1634
	Cu3p	Cu 3p	74.10 eV	0	3.05
Voigt doublet (split 2.49 eV, ratio 2)		77.05 eV	0	3.30	2916

^a For the background correction, the Shirley function is used. For peak fitting the Voigt function is used. Specifically for the Cu 3p there is also a Voigt doublet used. The binding energy (BE) is peak position in eV. The peak area is calculated by KolXPD. Lwid is the Lorentzian width within the Voigt function. Gwid is the Gaussian width within the function. The split in the Voigt Doublet function is the distance between the two peaks in eV. The ratio in the Voigt doublet is the ratio between the two peak areas. An energy calibration was performed using an Au reference. The Au 4f peak was observed at 83.8 eV (reported 84.0 eV). The offset of -0.2 eV is not taken into account in the values given here.

Table S2. The composition of the different ECD baths used in this manuscript

	Conc. in blank-bath	Conc. in formaldehyde-bath	Conc. in copper- bath	Conc. in ECD- bath
CuSO ₄ .5H ₂ O	-	-	12.48 g.L ⁻¹ (0.05 M)	12.48 g.L ⁻¹ (0.05 M)
HCOH (37% in H ₂ O)	-	8 mL.L ⁻¹ (0.1 M)	-	8 mL.L ⁻¹ (0.1 M)
EDTA	29.22 g.L ⁻¹ (0.1 M)	29.22 g.L ⁻¹ (0.1 M)	29.22 g.L ⁻¹ (0.1 M)	29.22 g.L ⁻¹ (0.1 M)
2,2'-bipyridyl	20 mg.L ⁻¹	20 mg.L ⁻¹	20 mg.L ⁻¹	20 mg.L ⁻¹
pH (adjusted with NaOH)	12.4	12.4	12.4	12.4

Table S3. Comparison between reported electrocatalysts for ethanol oxidation

Journal	Material	Conditions	Peak current density (mA _{mg_{Pd}} ⁻¹)	Ref
Our work	Pd ₅ -Cu ₈ /C	1.0 M KOH + 1.0 M ethanol, 50 mVs ⁻¹	2833	-
<i>ACS Appl. Mater. Interfaces</i>	Pd-WC/GN	1.0 M KOH + 1.0 M ethanol, 50 mVs ⁻¹	2349	S1
<i>Electrochimica Acta</i>	Pd _{5,0} Sn/CNT	1.0 M KOH + 1.0 M ethanol, 50 mVs ⁻¹	3434	S2
<i>Applied Catalysis B: Environmental</i>	Pd-Ni/C	0.1 M KOH + 0.5 M ethanol, 50 mVs ⁻¹	2010	S3
<i>Applied Catalysis B: Environmental</i>	PdP ₂ /rGO	0.5 M KOH + 0.5 M ethanol, 50 mVs ⁻¹	1600	S4
<i>ACS Appl. Mater. Interfaces</i>	PdCu ₂ -2	1.0 M KOH + 1.0 M ethanol, 50 mVs ⁻¹	1630	S5
<i>Langmuir</i>	Pd ₂₁ Cu ₇₉	0.5 M KOH + 0.5 M ethanol, 20 mVs ⁻¹	1782	S6
<i>Nanoscale</i>	PdCu/3DGS	1.0 M KOH + 1.0 M ethanol, 50 mVs ⁻¹	1140	S7
<i>Nanoscale Research Letters</i>	Pd-Cu _(F) /RGO	0.5 M NaOH + 0.5 M ethanol, 20 mVs ⁻¹	2416	S8
<i>New Journal of Chemistry</i>	Pd ₁ Fe ₁ /CNF	1.0 M NaOH + 1.0 M ethanol, 50 mVs ⁻¹	2158	S9

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