

Supporting Information

Palladium Particles Modified by Mixed-Frequency Square-Wave Potential Treatment to Enhance Electrocatalytic Performance for Formic Acid Oxidation

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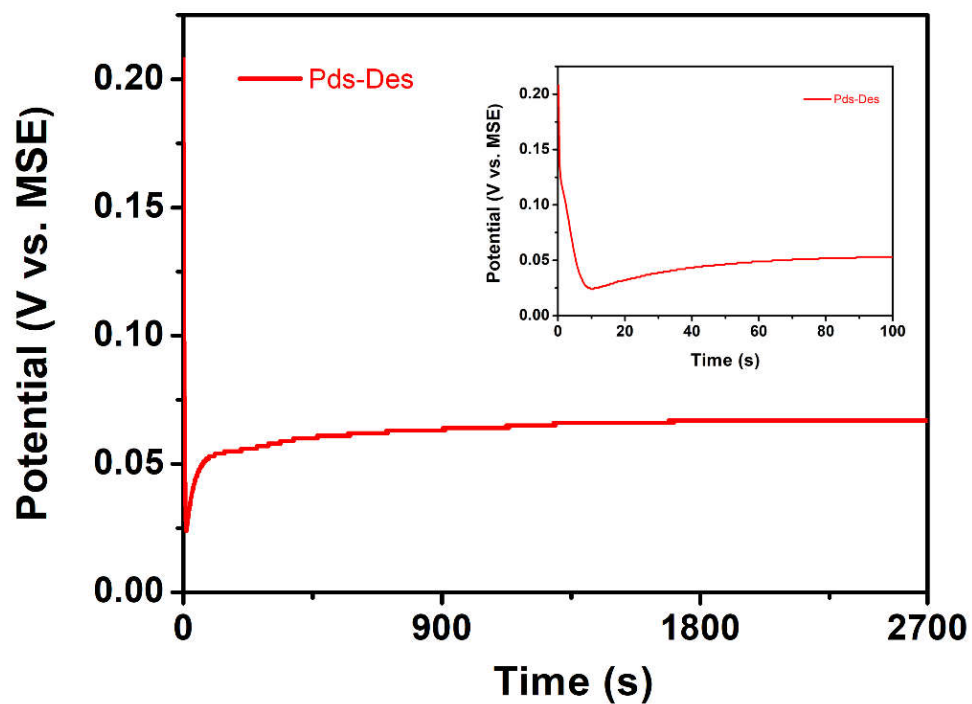


Figure S1. Chronoamperograms measured during electrodeposition at -0.15 mA cm^{-2} for 2700 s.

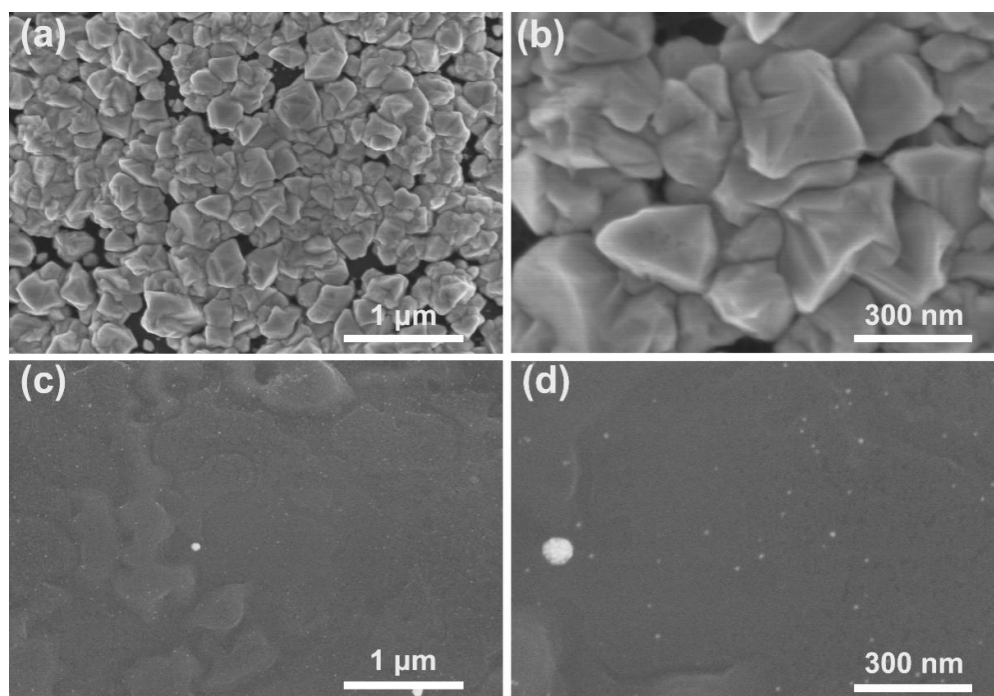


Figure S2. a) Low-magnification SEM image and b) high-magnification SEM image of Pd particles electrodeposited for 2700 s at -0.30 mA cm^{-2} ; c) low-magnification SEM image and d) high-magnification SEM image of Pd particles electrodeposited for 2700 s at -0.05 mA cm^{-2} .

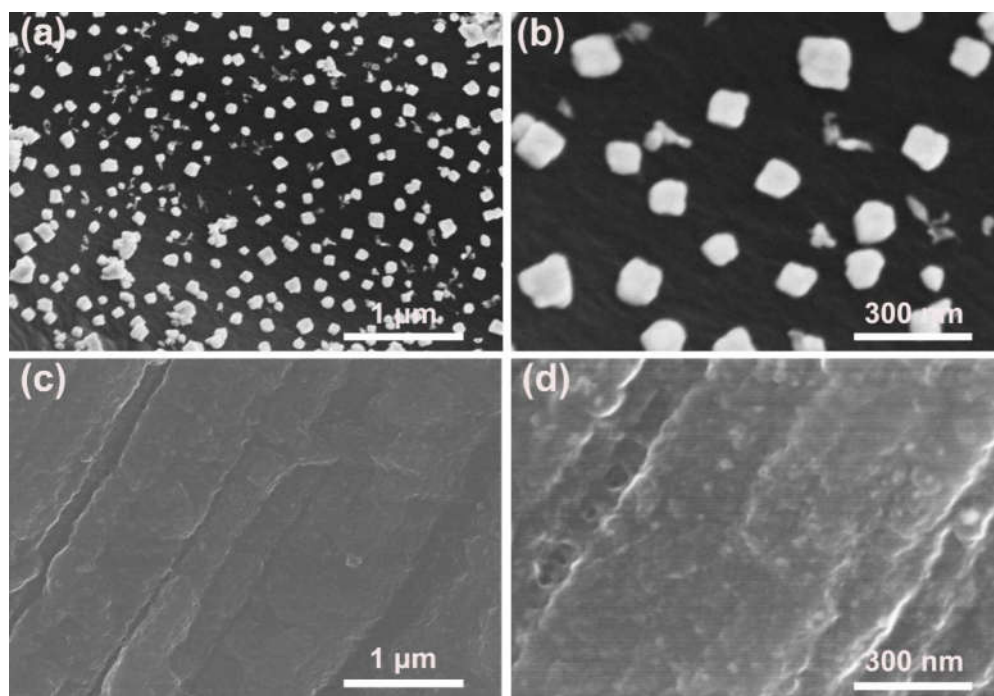


Figure S3. a) Low-magnification SEM image and b) high-magnification SEM image of Pd electrodeposited at -0.15 mA cm^{-2} for 2700 s on carbon paper and then treated by square-wave potential between 0.6 V and -3.2 V for 2 h with a frequency of 10 Hz in 1 M H_2SO_4 solution; c) low-magnification SEM image and d) high-magnification SEM image of Pd particles electro-deposited at -0.15 mA cm^{-2} for 2700 s and then square-wave potential between 0.6 V and -3.2 V for 4 h with a frequency of 10 Hz in 1 M H_2SO_4 solution.

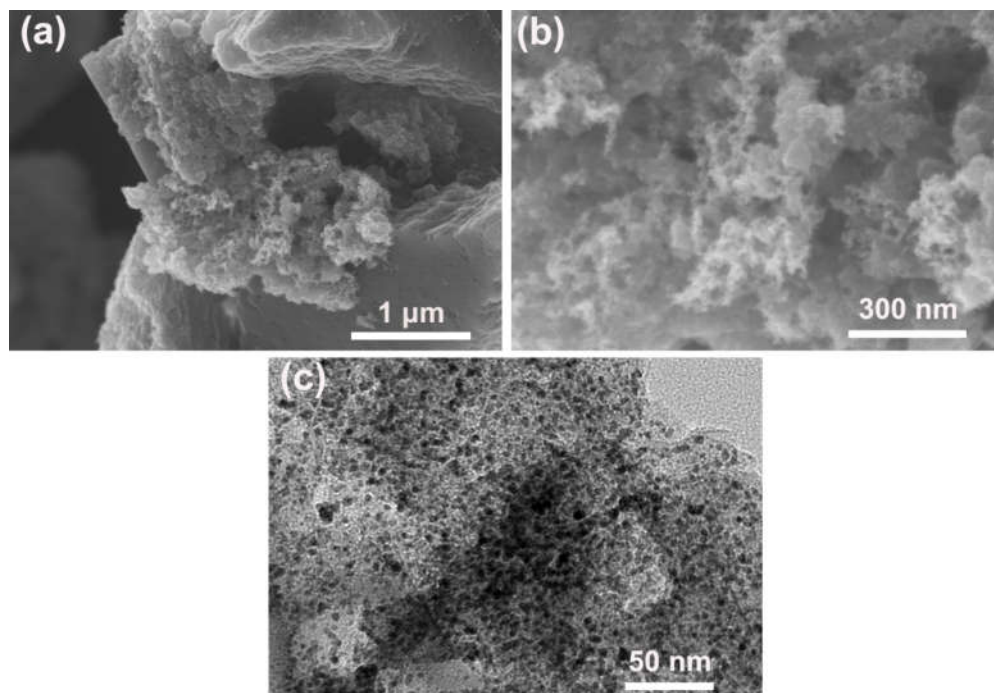


Figure S4. a) Low-magnification SEM image; b) high-magnification SEM image; c) TEM image of Pd/C.

Table S1. Comparison between Pds–Mixed and state-of-the-art Pd-based catalysts in terms of catalytic current toward FAO a scan rate of 50 mV s^{−1}.

Sample	The condition of test toward FAO	The composition of catalyst	The amount of catalyst	Current peak	Reference
Pds–Mixed	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	Pd particles	0.038 mg	1.43 A mg ^{−1}	this work
H–Pd–3	0.5 M HClO ₄ + 0.5 M HCOOH	H–Pd-3/Ketjen carbon (EC300J)	/	1.8 A mg ^{−1}	[1]
Pd _{1.1} /WO _{2.72}	0.1 M HClO ₄ + 0.1 M HCOOH	Pd/WO _{2.72} /KetjenBlack EC-300-J carbon	0.04 mg	1.615 A mg _{Pd} ^{−1}	[2]
Freestanding Pd nanosheets	0.5 M H ₂ SO ₄ + 0.25 M HCOOH	41 nm hexagonal Pd nanoplates	/	1.38 A mg ^{−1}	[3]
Twisted palladium–copper nanochains	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	Tcs-PdCu/XC-72 carbon	about 0.006 mg	1.1 A mg _{Pd} ^{−1}	[4]
PdH _{0.43} -200 °C	0.5 M H ₂ SO ₄ + 0.25 M HCOOH	PdH _{0.43} -200 °C	0.005 mg	1.06 A mg ^{−1}	[5]
3D graphene hollow nanospheres@palladium-networks	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	3D graphene hollow nanospheres@palladium-networks	0.012 mg	0.97 A mg _{Pd} ^{−1}	[6]
Pd/NYPA–MWCNTs	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	Pd/NYPA–MWCNTs	0.01 mg	0.954 A mg _{Pd} ^{−1}	[7]
Pd ₄ Sn nanochain networks	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	Pd ₄ Sn nanochain networks + XC-72 carbon	0.012 mg	0.85 A mg _{Pd} ^{−1}	[8]
Pd ₃ Fe/C	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	Pd ₃ Fe/C	about 0.012 mg	0.696 A mg ^{−1}	[9]
Pd ₁ Cu ₃ /CNTs	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	Pd ₁ Cu ₃ /CNTs	/	0.56 A mg ^{−1}	[10]
Pd/NS–G	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	Pd/NS–G	/	0.502 A mg ^{−1}	[11]
Pd ₃ Pt half-shells	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	Pd ₃ Pt half-shells	0.012 mg	0.318 A mg ^{−1}	[12]

Pd@graphene	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	Pd@graphene	0.01386 mg	0.0895A mg ⁻¹	[13]
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Abbreviations:

Tcs-PdCu: twisted PdCu nanochains; NYPA: naphthalen-1-ylmethylphosphonic acid; MWCNTs: multiwall carbon nanotubes; CNTs: carbon nanotubes; NS-G: N and S dual-doped graphene.

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