SUPPORTING INFORMATION

Palladium nanoparticles in polyols: synthesis, catalytic couplings and hydrogenations

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Table S1. Summary table of monometallic Pd-based NPs synthesis in polyols.

Reaction conditions	Size	Morphology and structure	Ref.[a]
$PdCl_2$, H_2O, EG 100 °C, 1 h	6.0±0.5 nm	Spherical with monoalkoxide species at the surface	40
Na_2PdCl_4, PVP, EG (M_w=55000 g.mol^{-1}), 110 °C in air, 8 h	10 nm	Uniform cubooctahedral	41
H_2PdCl_4 (prepared from $PdCl_2$ and $HCl_{aq.}$), PVP EG, 160 °C, 3 h	5 to 17 nm	Icosahedra	43
Na_2PdCl_4, PVP, Na_2SO_4, DEG, 105 °C, 3 h	5-15 nm	Decahedra	44
Na_2PdCl_4, $HCl_{aq.}$, PVP, DEG, 105 °C, 3 h	6-25 nm	Icosahedra	44
Na_2PdCl_4, PVP (M_w=55000 g.mol^{-1}), EG or DEG, 140 °C, 3 h	6 nm	Truncated octahedral EG or icosahedra DEG	45
Na_2PdCl_4, $NaCl_{aq.}$, EG, PVP, (M_w=360000 g.mol^{-1}), in air, 120 °C, 48 h	tailored 15-42 nm	Icosahedral	46
$PdCl_2$ or Na_2PdCl_4 $AgNO_3$ or, $FeCl_3$ and NaI used to control the size and shape HCl, EG, 160°C, 1 h, PVP Mw= 50,000	10-20 nm	Spherical	47
2 solutions of Na_2PdCl_4 in EG and PVP in EG stirred for 2 h. Then both solutions were	Without additives, mean diameter ca. 5-8 nm.	Without additives, spherical.	48

periodically added and mixed each 30 s for 5 min at 160°C. Studies on the effect of additives $AgNO_3$ with different concentrations $FeCl_3$ and NaI	With additives, different sizes were observed: 1- 5-8 nm 2- 20 nm 3- 22 nm 4- 24 nm 5- 8-14 nm	With additives, different morphologies were observed: 1- spheres 2- cubes 3- tetrahedrons 4- octahedrons 5- nanorods	
H_2PdCl_4, PVP (Pd/PVP=1:10), EG, 190 °C, 2 h	3.2-53. nm	Spherical Pd NPs	49
$Pd(OAc)_2$, PVP (Pd/PVP=1:3.5), EG 160°C, 1 h	100 nm length 8.5 nm diameter	Nanochains	50
K_2PdCl_4, PVP (Pd/PVP=1:100, EG, 90°C, 2 h, in air	2.6±0.3 nm).	Quasi-spherical	51
$K_2[PdCl_4]$, PVP, EG (11.5 $mmol.h^{-1}$mixing rate), then 150 °C both under conventional heating (30 min) or under microwave irradiation (55 s).	No size description	Pd small cuboctahedra under microwave irradiation Pd NPs rice-shaped particles	52
H_2PdCl_4/CTAB/PVP (1:4:4), TEG, microwave (900 W), 80 s	23.8 nm	Nanocubes and nanobars	53
Aqueous solutions of CTAB and H_2PdCl_4 were added to PVP/EG at 150 °C, 30 min	Average aspect ratios of 7.8 (length, 18.3±1.6	Nanorods	54

	nm; width, 2.5±0.3 nm) and 2.5 (length, 6.5±0.7 nm; width, 2.7±0.3 nm),		
Na_2PdCl_4, $HCl_{aq.}$, PVP (Pd/PVP=1:5), EG, rt, addition of $FeCl_3$/EG solution at 85 °C, 4.5 h in air	triangular nanoplates of 28 nm in edge length	Triangular (majority) and hexagonal nanoplates, cubooctahedral and twinned nanoparticles	55
Aqueous solutions of $PdCl_2.2NaCl.3H_2O$ poly(oxyethylene(20)sorbitan monolaurate) (Tween20), or poly(ethylene(40)glycol monostearate) as stabilizers 10 min sonication, rt	5 nm (Tween20) 14 nm (PEG40-MS)	Spherical	57
$PdCl_2$, HCl, PVP/EG or PVP/glycerol; [Metal]=10 mM - microwave irradiation at 198 °C for EG and 250 °C for glycerol, 10-15 min - microwave irradiation (700 W), 10 min - microwave irradiation under continuous-flow (1 mL/min), 198 °C for EG	 11 nm (EG) 11 nm (Glycerol) 10 nm (EG) 10 nm (Glycerol) 6.7 nm (EG)	Pd NPs nearly spherical in shape (i.e., cuboctahedra and icosahedra)	56

$Pd(NO_3)_2$, PVP, EG ultrasonic irradiation (50 kHz), 180 min	3-6 nm	Spherical	58
Na_2PdCl_4 (5 and 50 mM aq. solutions), glycerol monooleate (70 and 60 wt%), rt, 24 h	4.9±1.6 nm	Spherical	65
Na_2PdCl_4 (aq. solution), PVP (M_w=29000 g.mol^{-1}), glycerol, 100 °C, 3 h Supported on carbon black (Vulcan XC-72), adjusted pH 2	59.8 nm for 46.0%, 68.4 nm for 21.6%, and 57.5 nm for 32.4%	Pd NPs triangular hexagonal plate, and decahedron.	66
$PdCl_2$, PVP (M_w=55,000 g.mol^{-1}, 0.045 M), glycerol, 290 °C, from 2 min to 1h under microwave irradiation	9.6 nm for Pd NPs and 2 nm under microwave irradiation	Spherical under conventional heating Triangular nanoprisms under microwave irradiation	67
$PdCl_2$, $CTAB_{aq.}$, PVP or SDS, glycerol, 100 °C, 2 min under microwave irradiation and a maximum pressure of 280 psi.	5−15 nm (PVP) 3−5 nm (CTAB)	Spherical	68
Synthesis within Liposomal Nanoreactors: $PdCl_2$, NaCl, PBS (pH 7.4), glycerol lipid formulations (DPPC, DPPG, DOPE, or DOPG), 25 °C, 24 h, under Ar	(5% glycerol) 14±7 nm; (10% glycerol) 4±1, and 7±2 nm (20% glycerol) 3±1 nm	Amorphous without a well-defined shape	69
Solution-Based Synthesis:	Citrate DOPG liposomes	Triangular- and decahedron shaped	69

$PdCl_2$, sodium citrate or $NaBH_4$, PBS (pH 7.4), glycerol, 25 °C, 24 h in a temperature-controlled shaker (400 rpm)	11±4 nm		
	$NaBH_4$ DOPG liposomes, 5±2 nm	Heterogeneous population	
	Glycerol DPPC liposomes, 16±2 nm	Spherical	
	Glycerol DPPG liposomes, 4 ± 2, 16 ± 6 nm	Irregular shapes	
	Glycerol DOPE liposomes 9 ± 3 nm	Irregular shapes	
	Glycerol DOPG liposomes 2.6 ± 0.7 nm	Spherical	

$[PdCl_2(COD)]$, $Pd(OAc)_2$, [Pd(ma)(nbd)] or $[Pd_2(dba)_3]$; TPPTS (Pd/TPPTS 1:1), glycerol, 80 °C overnight under H_2 (3 bar)	4.1±1.4 nm $Pd(OAc)_2$ 3.5±1.3 nm $[PdCl_2(COD)]$	Spherical for $[PdCl_2(cod)]$ and $Pd(OAc)_2$ Irregular shapes with [Pd(ma)(nbd)] and $[Pd_2(dba)_3]$	74
$Pd(OAc)_2$ or $[PdCl_2(COD)]$, *N*-alkylated PTA-based ligands (Pd/L 1:1), 60 °C, overnight under H_2 (3 bar)	3.2±0.8 nm	Well-dispersed spherical NPs for *N*-benzyl PTA ligand with $[PdCl_2(COD)]$	76
$[PdCl_2(COD)]$, $Pd(OAc)_2$ or $[Pd_2(dba)_3]$; cinchonidine, cinchonine, quinine or quinidine; glycerol, 80 °C, 18 h, H_2 (3 bar)	2.1±0.6 nm cinchonidine/$Pd(OAc)_2$ 1.4±0.3 nm quinidine/ $Pd(OAc)_2$ 1.6±0.3 nm quinidine/ $[PdCl_2(COD)]$ 1.5±0.3 nm cinchonidine /$[Pd_2(dba)_3]$	Spherical in all cases	79

[a] References match the reference numbering used in the main text.

Table S2. Summary table of polymetallic Pd-based NPs synthesis in polyols.

Pd-based NPs	Reaction conditions	Size	Morphology and structure	Ref.[a]
AgPd	$AgNO_3$, $Pd(NO_3)_2$, PVP (M_w=10000 g.mol^{-1}), EG 120°C, 4h	7 nm $Ag_{70}Pd_{30}$	AgPd alloy, quasi-spherical shape	89
AuPd	$PdCl_2$ and $HAuCl_4$, EG, 1 h under N_2 and microwave irradiation (900 W, cycling mode: 21 s on, 9 s off)	Pd shell 3 nm, and Au core 9 nm.	(Au)core–(Pd)shell Spherical particles	90
AuPd	Na_2PdCl_4 ($5\cdot10^{-4}$ mol/L), $NaAuCl_4$ ($5\cdot10^{-4}$ mol/L), PVP (0.1 wt%), EG or glycerol (2% water content) 1h, in air under microwave irradiation (800 W, cycling mode: 15 s on, 5 s off)	15 nm AuPd NPs	(Au)core–(Pd)shell	91
AuPd	$PdCl_2$ and PVP, EG, 140 °C in air until change of color. Then $HAuCl_4$ addition (aq. solution), 140 °C, 3 h in air	NPs <5 nm NPs > 5nm	AuPd NPs alloy. Core: AuPd NPs alloy intermediate layer Au rich, and a third (surface) layer Pd-rich	93
AgPd	$AgNO_3$, $Pd(NO_3)_2$, EG-H_2O, 190°C, 2 h in air	5.5 nm	Pd–Ag alloy Pd:Ag of ca. 3:1	96

AgPd	Addition of $PdCl_2$, hexadecylamine, dioctylether to $AgNO_3$, tri-*n*-octylphosphine in DEG or glycerol, 200 °C, 2 h	20.6±1.0 nm	AgPd alloy cuboctahedral structure	97
AgPd	$AgNO_3$, PVP, EG, 160 °C, 2 h. Then, slow addition of K_2PdCl_4, PVP, EG, 2 h	9.2 nm	AgPd alloy structure	98
PtPd	$PdCl_2$ and K_2PtCl_4, EG, 197 °C, 3 h in air	6±2 nm 7±2 nm agglomerates agglomerates	$Pd_{20}Pt_{80}$ $Pd_{40}Pt_{60}$ $Pd_{60}Pt_{40}$ $Pd_{80}Pt_{20}$ For <40 atomic% of Pd, Pd atoms are covered by Pt and, as such, cannot form surface oxides. This suggests Pt surface segregation.	99
PtPd	H_2PtCl_6, $AgNO_3$, PVP, 160°C, 15 min. To the previous solution of preformed PtNPs, addition of $AgNO_3$ in EG at 160 °C, followed by Na_2PdCl_4, PVP (slow addition), then 300 °C, 15 min.	10–16 nm 10–25 nm Pd shell 1–3.5 nm	PtPd NPs polyhedral Pt(core)–Pd(shell) NPs	101
PtPd	H_2PtCl_6, $AgNO_3$, PVP (Pt/PVP 2:1), 160 °C, 15 min under Ar.	15–25 nm thickness of the Pd <4 nm	Pt(core)–Pd(shell) NPs with truncated polyhedral morphologies	102,103

	To the previous solution of preformed PtNPs, addition of Na_2PdCl_4, PVP, 160 °C, 15 min, slow addition.			
PtPd	H_2PtCl_6, $AgNO_3$, PVP (Pt/PVP 2:1), 160 °C, 20 min. To the previous solution of preformed PtNPs, addition of K_2PdCl_4, PVP, 160 °C, 20 min, slow addition, then 285 °C, 15 min	13.5 nm, 8.5 nm(core) 2.5 nm (shell)	Pt(core)–Pd(shell) NPs with polyhedral morphology.	104
PtPd	Na_2PdCl_4, PVP (15 wt%), EG, 200 °C, 6 s under microwave irradiation in flow Preformed Pd NPs then mixed with $H_2[PtCl_6].6H_2O$ (Pd/Pt 3:1) in EG at pH 12 ($NaOH_{aq.}$), rt, 6–72 h	6.5 ±0.6 nm Pd NPs 6.5 ± 0.6 nm Pd@Pt core–shell NPs Pt shell thickness ca. 0.25 nm.	Spherical, Pd@Pt core–shell NPs	105
PtPd	Addition of $H_2PtCl_6 \cdot 6H_2O$/PVP in EG to a solution of $PdCl_2$ in HCl_{aq} at 198 °C (in EG) and 250 °C (in glycerol) under microwave irradiation:		All cluster in cluster structure in EG	106
	- Multimode 700 W, 2-3 min; then kept 10 min	Pt/Pd (1:1) 6.2 nm (EG) 9.3 nm (glycerol)	Spherical Spherical	

	- Single-Mode 300 W, 2-3 min; then kept 10 min	Pt/Pd (1:1) 5-9 nm (EG)	Spherical-like cubic	
	- Single-Mode in continuous flow	Pt/Pd (1:1) 5.9 nm (EG)	Spherical-like cubic	
RuPd, PtRuPd	Ru(core)Pd(shell): $RuCl_3$, Pd metal powder in HNO_3, PVP, EG, 160 °C, 2 h Pt/Ru(core)Pd(shell): Ru(core)Pd(shell), H_2PtCl_6, PVP, EG	Ru(core)Pd(shell): mean diameter ca. 3 nm Pt/Ru(core)Pd(shell): mean diameter ca. 3.6 nm	Ru(core)Pd(shell) and Pt/Ru(core)-Pd(shell) nanoparticles	[107]
PdRu	$RuCl_3$, K_2PdCl_4, TrEG, PVP, 200 °C, 40 min	Mean diameters in the range 6-10 nm. Ru-rich NPs exhibited non-spherical NPs	PdRu alloys exhibiting spherical nanoparticles, with both fcc and hcp phases coexisting in a single particle. Ru-rich NPs exhibited non-spherical morphology	[108]
PdRu	$RuCl_3$, Na_2PdCl_4, PVP, TrEG, 200 °C, 40 min	Mean diameters in the range 6-17 nm	PdRu alloys exhibiting spherical nanoparticles	[109]
PdRu	$RuCl_3$, Na_2PdCl_4, PVP, TrEG, 200 °C	Mean diameters in the range 6-16 nm	PdRu alloys exhibiting spherical nanoparticles	[110]

PdRu	$RuCl_3$, Na_2PdCl_4, PVP, TrEG, 200 °C, flow and semi-batch syntheses	Mean diameter ca. 10 nm	PdRu alloys exhibiting spherical nanoparticles	111
BiPd	$PdCl_2$, $Bi(NO_3)_3$, $NaBH_4$, PVP, TEG, 280 °C, 3 h	40-60 nm	Cube-shaped Bi_2Pd (and Bi_2PdO_4)	112
PdBiX (X = S or Se)	$Pd(OAc)_2$, $Bi(NO_3)_3$, EG, thiosemicarbazide, 220 °C, 20 min under microwave irradiation	$Pd_3Bi_2S_2$ and $Pd_3Bi_2Se_2$: ca. 50 nm	Spherical $Pd_3Bi_2X_2$ NPs (X = S or Se)	113
FePd	$Pd(acac)_2$, $Fe(CO)_5$, 1,2-hexadecanediol, n-adamantane carboxylic acid and tributylphosphine as stabilizers, 120-180 °C, 30-60 min	11 - 16 nm	Spherical NPs	115
FePd	$Pd(acac)_2$, $Fe(CO)_5$, 1,2-hexadecanediol, oleic acid and oleyl amine as capping agents, 259 °C, 10 min, and further annealing at 600 °C	ca. 8.4 nm	Spherical NPs	116
FePd	$Fe(acac)_3$, $Pd(OAc)_2$, oleic acid/oleylamine (1:1), EG (deoxygenated), 200 °C, 1h under N_2	5.3 ±1.1 nm	nearly spherical FePd alloy.	117
FePd	$Pd(acac)_2$, 1,2-hexadecanediol, oleic acid, oleylamine, or dodecanethiol in benzyl ether or toluene 100-120 °C, 30 min under Ar.	For Pd/Fe ratio (1.4:1) to (5:1), 4-8 nm	multi-twinned structures in several samples	118

	Then $Fe(CO)_5$ addition, 120 or 300 °C, 30 min			
Pd, PdCo	- $PdCl_2$, PVP, NH_3 aq., EG, 140 °C, a few min - $PdCl_2$, Co(acac)$_2$, PVP, EG, 120 °C, 30 min. Then NaOH, 180 °C, 10 min	7-10 nm 4−6 nm inner core 2−6 nm outer shell	Spherical NPs Spherical NPs with core−shell morphology	120
NiPd	Pd(OAc)$_2$ in dioxane added to $NiSO_4 \cdot 7H_2O$, PVP, EG at 80 °C. Then $NaOH_{aq}$ addition (pH 9-11), 197 °C for 15 min and reflux for 3 h under N_2	1.5-2.3 nm Ni/Pd(2/3) nanoclusters: 1.9 ±0.27 nm 20-30 nm	Spherical NPs, random alloy Spherical NPs, NiPd nanoalloys	121,122
NiPd	Ni(acac)$_2$, $(NH_4)_2PdCl_6$, TTAB (15:1, 30:1, 50:1), PVP, 1,5-pentanediol, 140 °C, 160 °C, or 180 °C, 20 min	Cube length 9–11nm	Nanocubes and nanorods Ni1Pd3 NPs and polyhedral Pd NPs only	123
CuPd	$CuSO_4 \cdot 5H_2O$, PVP in EG, H_2PdCl_6 in dioxane addition (pH 10, $NaOH_{aq.}$ addition) at 0-5 °C; then 198 °C, 3 h under N_2	1.7-2.3 nm CuPt NPs 1.0-1.3 CuPd NPs	Cu3Pd alloy cluster with spherical shape	124
CuPd	$CuSO_4 \cdot 5H_2O$, PVP in EG, Pd(OAc)$_2$ in dioxane addition (pH 10, $NaOH_{aq.}$ addition) at 0-5 °C; then 198 °C, 3 h under N_2	2.5-7.0 nm, Cu95Pd5 5.0-10.0 nm Cu90Pd10	Irregular shape consisting in multiple smallerparticles (“microclusters”) in an aggregated state.	125

		5.0-12.5nm Cu85Pd15 5.6 ±1.5 nm Cu/Pd(4/1)	Spherical CuPd alloy	
CuPd	[Cu(TMEDA)(μ-OH)]$_2$Cl$_2$, mesitylcopper(I), or Cu(OAc)$_2$ and Pd(OAc)$_2$, Pd$_2$(dba)$_3$, or [PdCl$_2$(COD)]; PVP (M_w=10000 g.mol^{-1}, Cu/Pd/PVP 1:1:40), glycerol, 120 °C, 12 h under H_2 (3 bar)	With CuTMEDA and Pd(OAc)$_2$ 3.8 ± 1.5 nm Cu1Pd1 2.5 ± 1.5 nm Cu2Pd1	PdNPs coated by a nonuniform Cu-shell disordered alloys	[126]

[a] References match the reference numbering used in the main text.