ELECTRONIC SUPPLEMENTARY INFORMATION

Core-Shell PdCu Bimetallic Colloidal Nanoparticles in Sonogashira Cross-coupling reaction: Mechanistic insights into the Catalyst Mode of Action

Drielly N. Olekszyszen,[a,b] Brunno L. Albuquerque,[a,c] Dagoberto de O. Silva,[a] Guilherme L. Tripodi,[d] Daniela C. de Oliveira[e] and Josiel B. Domingos*[a]

[a.] *LaCBio – Laboratory of Biomimetic Catalysis, Department of Chemistry, Federal University of Santa Catarina, Florianópolis - SC, 88040-900, Brazil; Tel: +55 48 37213620; E-mail: josiel.domingos@ufsc.br*
[b.] *Federal Institute of Paraná, Campus União da Vitória - PR, 84600-000, Brazil.*
[c.] *LAMOCA, Institute of Chemistry, Federal University of Rio Grande do Sul, Porto Alegre - RS, 91509-900, Brazil.*
[d.] *Institute for Molecules and Materials, Radboud University, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands.*
[e.] *Brazilian Synchrotron Light Laboratory, C. P. 6192, Campinas - SP, 13083-970, Brazil.*

Summary

Table S1 Pd and Cu composition determined by FAAS. 2

Fig. S1 Particles diameter histogram plots of catalysts samples. 2

Fig. S2 Overlaid XANES spectra at Pd K-edge for all samples. 3

Table S2 Refined distances (d/Å), and mean number of first neighbors (CN) in Pd_XCu_1 NP samples. 3

Fig. S3 XAFS functions in k-space of samples and reference foils at Pd and Cu K-edges 4

Table S3 Catalysts concentration in the Sonogashira reaction. 4

Table S4 RPKA experiments conditions (2 mmol K_2CO_3, 2 mol% Pd, 7.5 mL DMF, 80 °C, 180 min, Pd_2Cu_1 catalyst). 5

Fig. S5 RPKA experiments of the coupling between iodobenzene and phenylacetylene (conditions: Table S3 and 2 mmol K_2CO_3, 2 mol% Pd, 7.5 mL DMF, 80 °C, 180 min). 5

Fig. S6 Reaction kinetics profiles for phenylacetylene (PA) and iodobenzene (IB) or *p*-nitroiodobenzene (NIB) or *p*-methoxy iodobenzene (MIB) catalyzed by Pd_2Cu_1-NPs (conditions: 0.9 mmol phenylacetylene, 1.5 mmol iodobenzene, 2 mmol K_2CO_3, 2 mol% Pd, 7.5 mL DMF, 80 °C). 6

Fig. S7 XANES analysis at the Cu K-edge (**A**) and Pd K-edge (**B**) of the Sonogashira reaction medium at different reaction times with Pd_2Cu_1 catalyst. 6

Fig. S8 FFT of a single particle from Pd_2Cu_1-NPs catalyst after the reaction. 7

Fig. S9 ACPI(+)-HRMS spectrum of $[Cu(C8H5)+K]^+$ detected in the reaction medium 30 min after the start of the Sonogashira reaction with Pd_2Cu_1-NPs catalyst. 7

Table S1 Pd and Cu composition determined by FAAS.

Catalyst	Pd:Cu ratio (mol%)	% metals (m m^{-1})
Pd_1Cu_1-NPs	$Pd_{42}Cu_{58}$	17% Pd; 14% Cu
Pd_2Cu_1-NPs	$Pd_{63}Cu_{37}$	26% Pd; 9% Cu
Pd_4Cu_1-NPs	$Pd_{79}Cu_{21}$	25% Pd; 4% Cu
Pd-NPs	Pd_{100} Cu_0	30% Pd

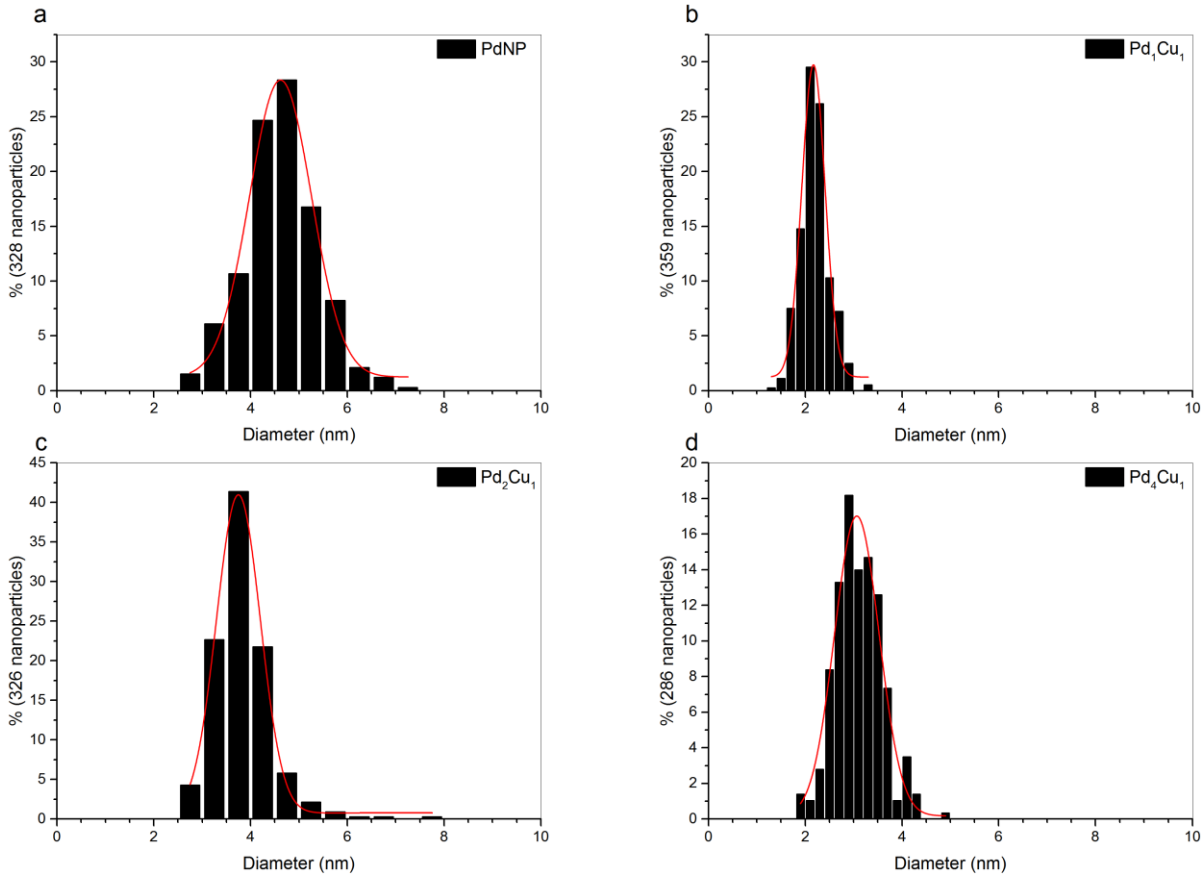


Fig. S1 Particles diameter histogram plots of catalysts samples.

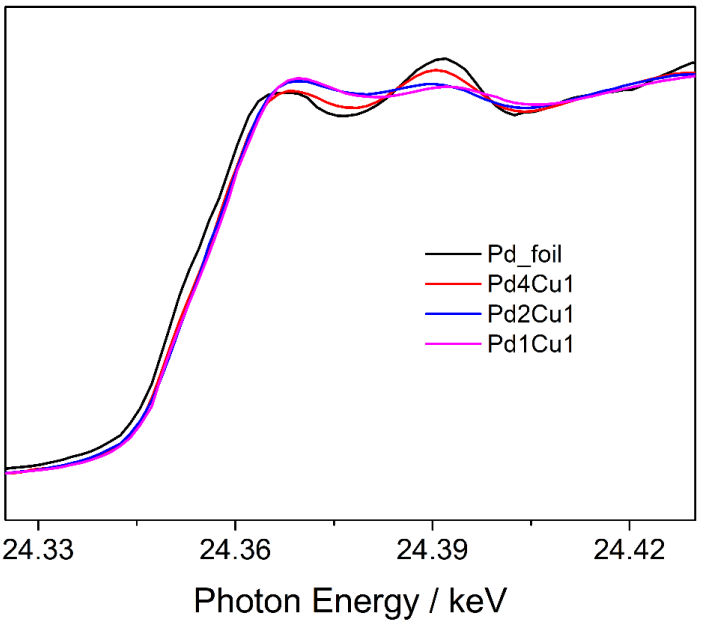


Fig. S2 Overlaid XANES spectra at Pd K-edge for all samples.

Table S2 Refined distances (d/Å), and mean number of first neighbors (CN) in Pd_xCu_1 NP samples.

	catalyst	**d (Pd-Pd) (Å)[i]**	**N[ii]**	**d (Pd-Cu) (Å)[iii]**	**N**	**d (Pd-O) (Å)**	**N**
Pd K-edge	Pd_1Cu_1	2.70(4)	4.1	2.62(0)	5.8	2.00(0)	2.2
	Pd_2Cu_1	2.70(3)	5.0	2.61(5)	2.6	1.97(2)	2.3
	Pd_4Cu_1	2.71(4)	9.3	2.63(4)	2.6	-	-
		d (Cu-Cu) (Å)	**N**	**d (Cu-Pd) (Å)**	**N**	**d (Cu-O) (Å)**	**N**
Cu K-edge	Pd_1Cu_1	2.62(0)	1.7	2.62(7)	1.3	1.92(0)	0.8
	Pd_2Cu_1	2.59(0)	1.0	2.61(5)	2.0	1.92(1)	1.0
	Pd_4Cu_1	2.55(3)	0.6	2.62(6)	5.0	1.89(1)	1.0

(i) The standard deviations in parentheses were obtained from k2-weighted least-squares refinements of the EXAFS function χ(k) and do not include systematic errors of the measurement ; atomic distances for Pd-Pd bulk is 2.752 Å and for Cu-Cu bulk is 2.553 Å; (ii) The estimated error of the N values is ca. 25%; the N for Pd and Cu bulk is 12; (iii) Pd-Cu and Cu-Pd distances were restricted to be the same, within the errors.

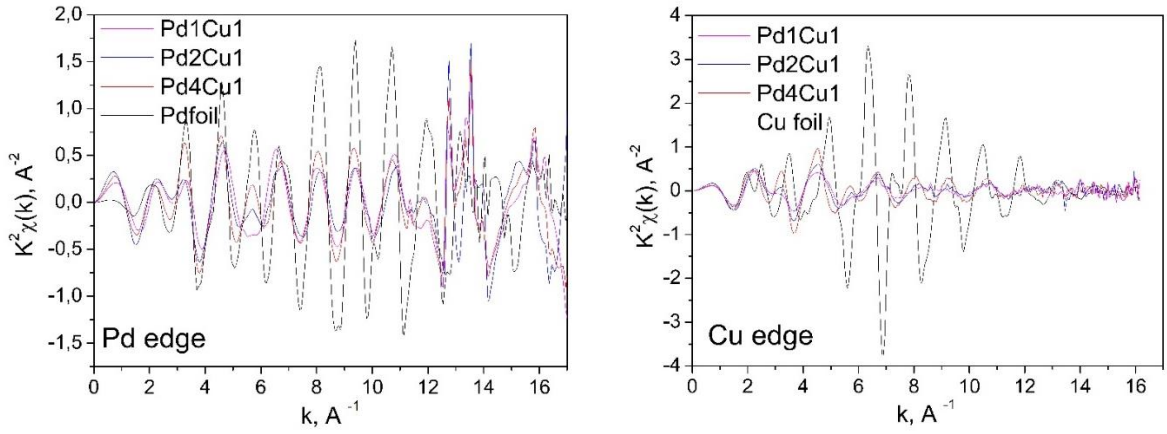


Fig. S3 XAFS functions in k-space of samples and reference foils at Pd and Cu K-edges

Table S3 Catalysts concentration in the Sonogashira reaction.

Catalyst	mol% Pd	mol% Cu	% PA	% DPA	% DPB
Pd_1Cu_1	2.0	2.7	38	33	5
Pd_2Cu_1	2.0	1.1	0	79	4
Pd_4Cu_2	2.0	0.5	0	67	3
Pd	2.0	0.0	33	26	2

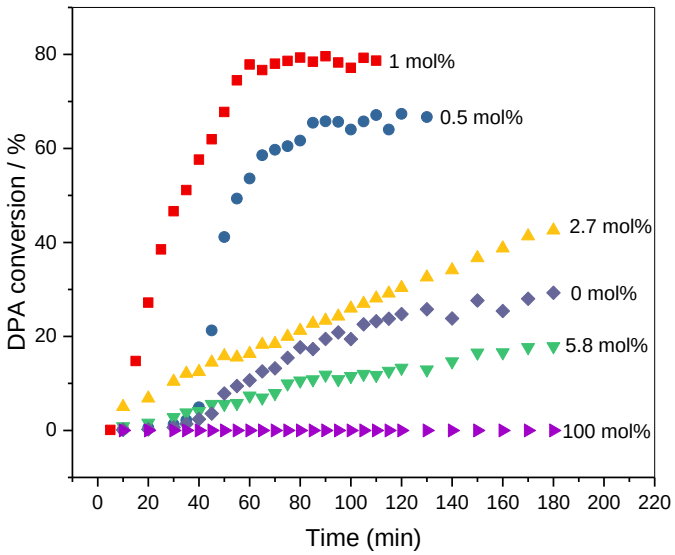
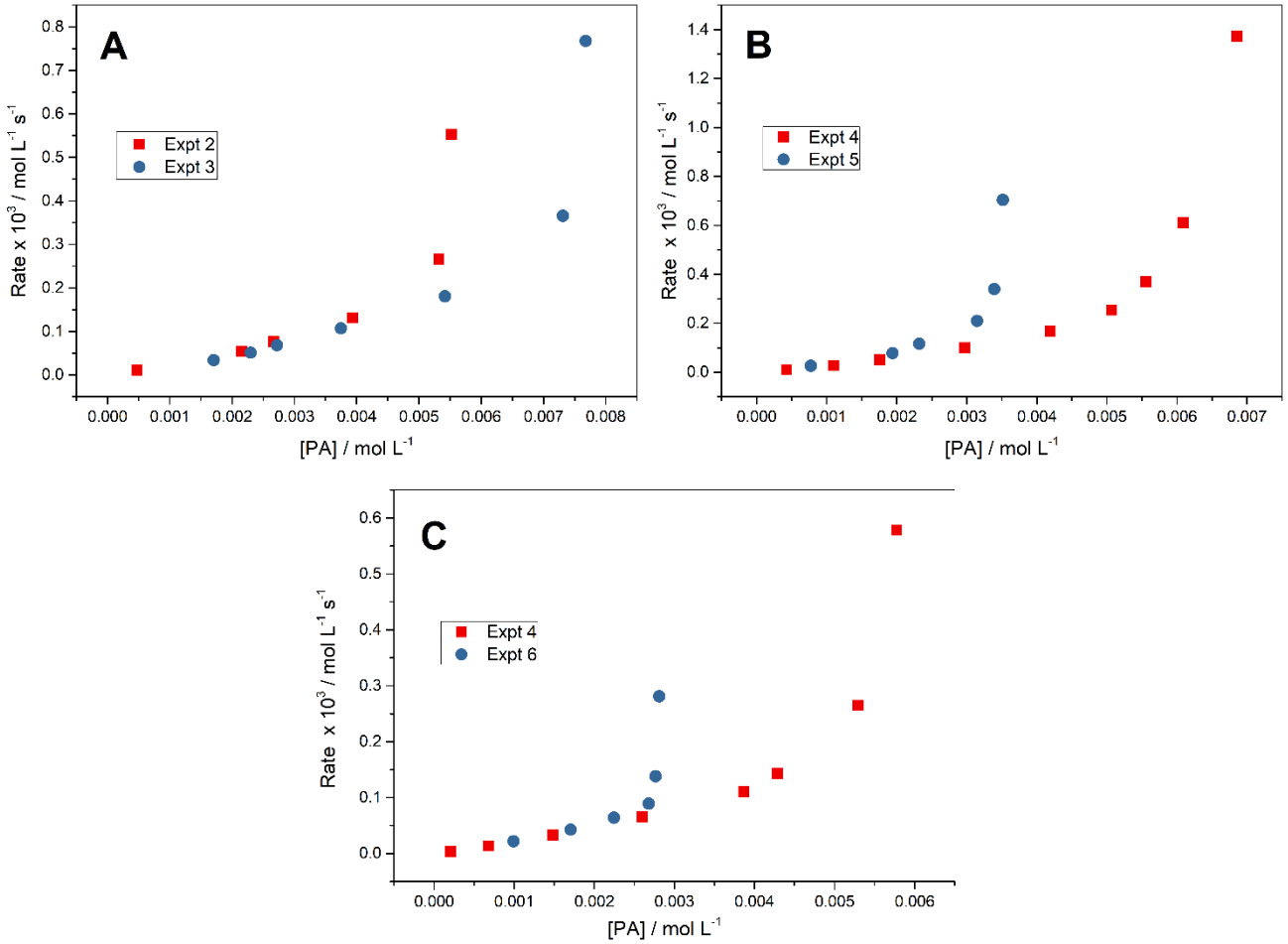


Fig. S4 Kinetic monitoring of the coupling between iodobenzene and phenylacetylene (DPA conversion) for different Cu concentrations applying the PdCu-NPs (conditions: 0.9 mmol phenylacetylene, 1.5 mmol iodobenzene, 2 mmol K_2CO_3, 2 mol% Pd, 7.5 mL DMF, 80 °C).

Table S4 RPKA experiments conditions (2 mmol K_2CO_3, 2 mol% Pd, 7.5 mL DMF, 80 °C, 180 min, Pd_2Cu_1 catalyst).

		[PA] (mol L^{-1})	[IB] (mol L^{-1})	[DPA] (mol L^{-1})	[DPB] (mol L^{-1})	[Pd] (µmol L^{-1})	[*e*][1] (mmol L^{-1})	PLOTS (Fig. S5)
Expt 1	Standard Condition	0.12	0.2	-	-	2	0.08	(A) Rate vs. [PA]
Expt 2	Standard Condition	0.12	0.2	-	-	2	0.08	
Expt 3	Reaction A	0.16	0.24	-	-	2	0.08	
Expt 4	Standard Condition	0.12	0.2	-	-	2	0.08	(B) Rate vs. [PA] + DPA (C) Rate vs. [PA] + DPB
Expt 5	Reaction B	0.06	0.14	0.06	-	2	0.08	
Expt 6	Reaction C	0.06	0.14	-	0.03	2	0.08	

[1]Excess of one substrate over another.



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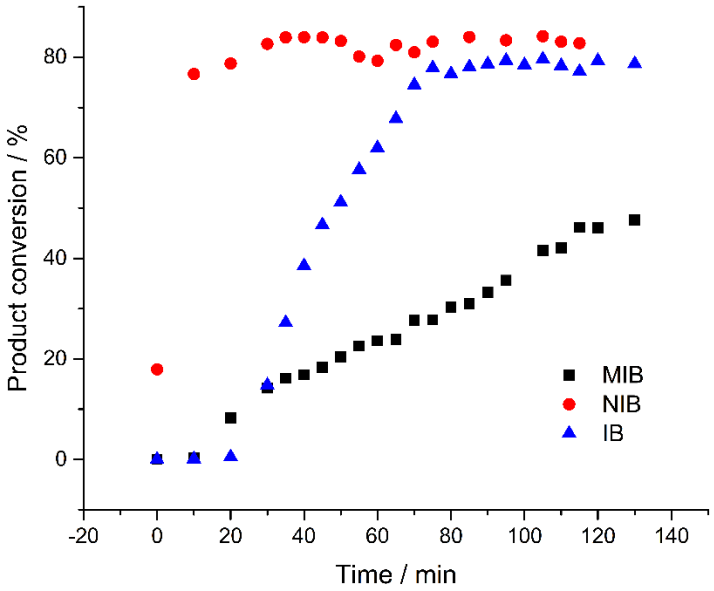
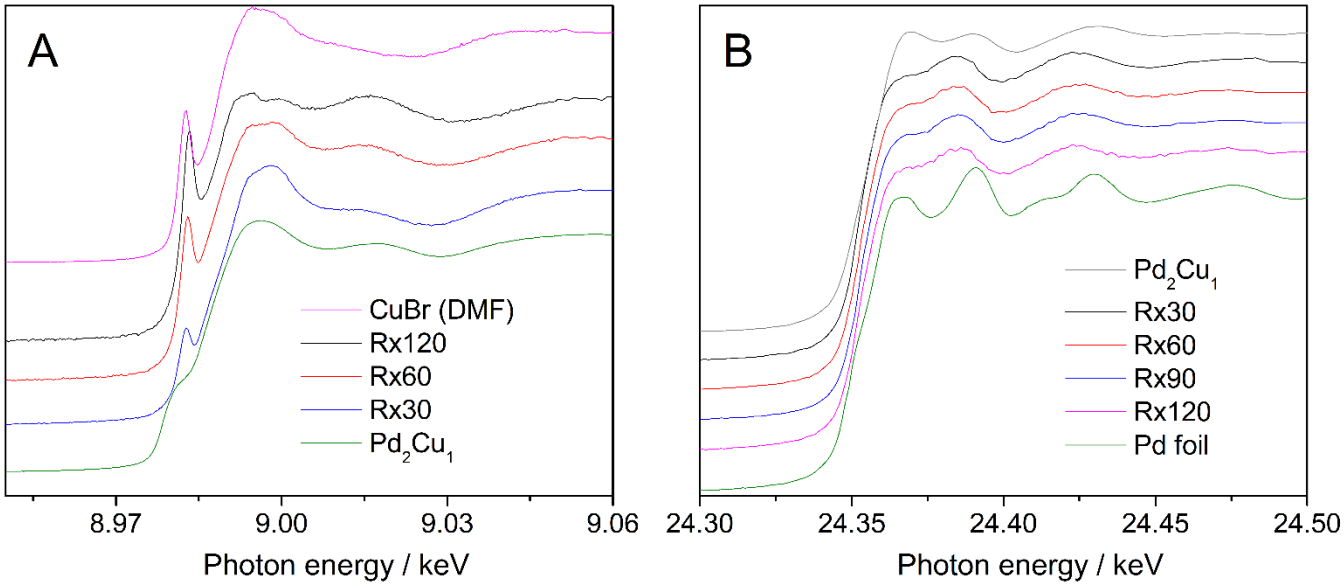


Fig. S6 Reaction kinetics profiles of product formation for the reaction of phenylacetylene (PA) with iodobenzene (IB) or *p*-nitroiodobenzene (NIB) or *p*-methoxy iodobenzene (MIB) catalyzed by Pd_2Cu_1-NPs (conditions: 0.9 mmol phenylacetylene, 1.5 mmol iodobenzene, 2 mmol K_2CO_3, 2 mol% Pd, 7.5 mL DMF, 80 °C).



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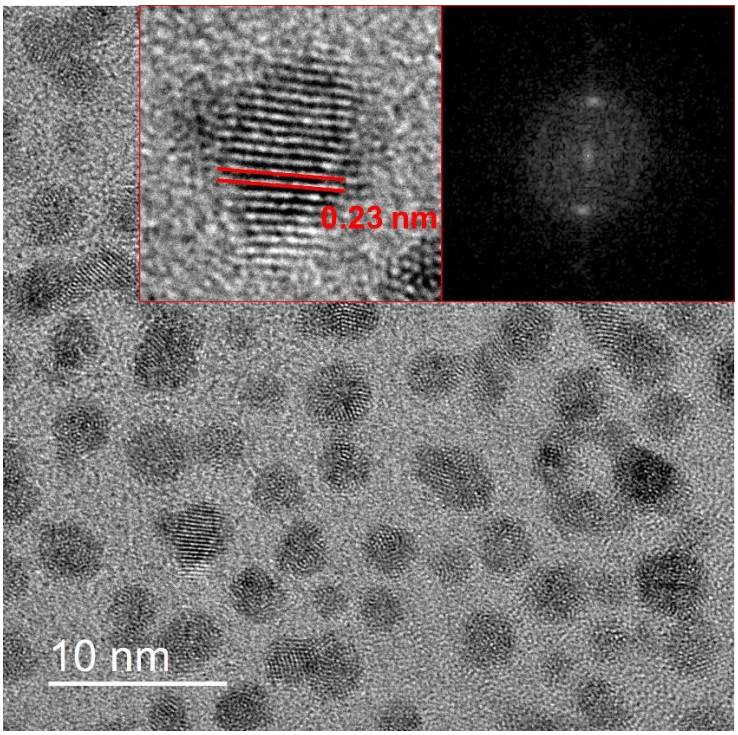

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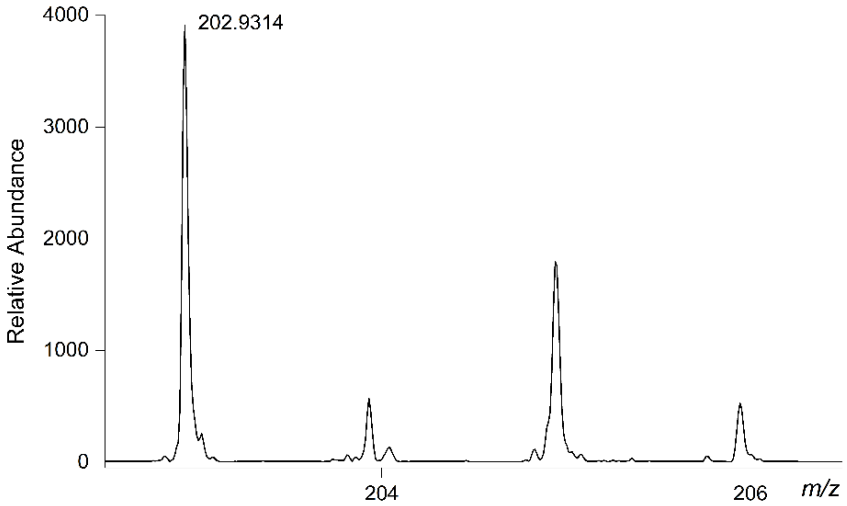

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