

Electronic Supplementary Information (ESI)

Is CO adequate to facilitate the formation of Pt₃M (M = Fe, Ni and Co) nanocubes?

Yuxuan Wang,^a Zhaoyong Sun,^b Amar Kumbhar,^c Zhiping Luo,^d Chenyu Wang,^b Jun Zhang,^{b,e}
Nathan Porter,^b Changmingzi Xu,^b Kai Sun,^f Benjamin Martens^a and Jiye Fang*^{a,b}

Email. jfang@binghamton.edu

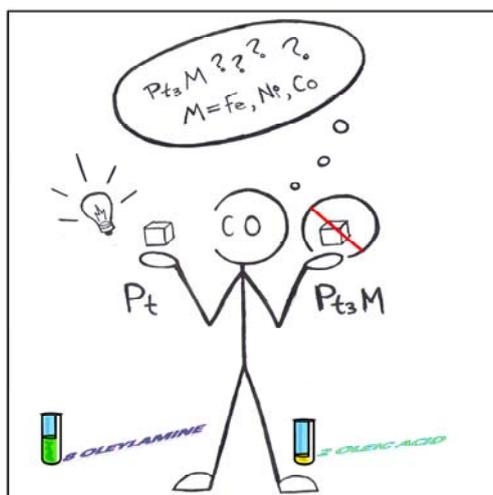
^aMaterials Science and Engineering Program, ^bDepartment of Chemistry, State University of New York at Binghamton, Binghamton, New York 13902, USA

^cChapel Hill Analytical and Nanofabrication Laboratory, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, USA

^dMicroscopy and Imaging Center and Materials Science and Engineering Program, Texas A&M University, College Station, Texas 77843, USA; Present address: Department of Chemistry and Physics, Fayetteville State University, Fayetteville, North Carolina 28301, USA

^ePresent address: Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois 60439, USA

^fDepartment of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, USA



Experimental Section

Chemicals: Cobalt (II) acetate tetrahydrate (99.999%), iron (II) chloride tetrahydrate (99.99%), oleic acid (90%), and oleylamine (70%) are Aldrich products. Formic acid (88%) and sulfuric acid (98%) were received from J. T. Baker. Nickel (II) acetylacetonate hydrate (97%), Platinum (II) acetylacetonate (49.3-49.8% Pt), anhydrous ethanol (200 proof), and anhydrous hexane (98.5%) were purchased from Alfa Aesar, Gelest, AAPER, and BDH, respectively. All chemicals were used without further purification.

Generation of freshly prepared gaseous CO: A three-neck flat-bottom flask containing a sufficient amount of concentrated sulfuric acid was placed in a water bath. The flask was connected to another reaction flask through a tubular desiccator fully filled sodium hydroxide and a glass tube with a sharp-tip at the other end (refer to **Scheme 1**). A separating funnel containing formic acid was equipped on the flat-bottom flask. Gaseous CO was produced by dropping formic acid into concentrated sulfuric acid under vigorous stirring at ~60 °C and the flow rate of CO stream can be controlled by tuning the addition rate of formic acid (Caution: carbon monoxide is extremely poisonous, and the whole setup should be placed in a fuel hood with a CO-detector equipped in the lab). The system was pre-flushed using argon followed by a stream of helium.

Preparation of Pt NCbs: To prepare Pt NCbs, the synthesis was carried out in two different ways, “heating mantle” and “hot oil-bath”. In a typical “heating mantle” process, 0.020 g (0.05 mmol) of platinum(II) acetylacetonate, 8.0 ml of oleylamine and 2.0 ml of oleic acid were pre-mixed in a three-neck round-bottom flask equipped with a condenser and a temperature-control system. The flask was also attached to a vacuum line and to the CO channel by immersing the sharp-tip of the CO tube into the mixed suspensions. The precursor mixture was first pre-heated to 100 °C with vigorous agitation under an argon stream to allow sufficient dissolution, and subsequently flashed using a helium stream to remove residual air

possibly remaining in the upper layer of the system when it was cooled to room temperature. To complete the synthesis, the resultant solution was bubbled with CO for 10min, and then re-heated to 200 °C (or 240 °C) at a heating rate of *ca.* 7.5 °C min⁻¹ under a continuing CO flow (*ca.* 35 cm³ min⁻¹) and gentle stirring. The reaction was ceased after a reflux for additional 5 min at 200 °C (or 240 °C) by the rapid removal of the heating mantle. The resultant product was isolated by centrifugation and washed with anhydrous ethanol for two cycles, and stored in hexane. The synthetic recipe in a “hot oil-bath” process is the same as mentioned above. The only difference is that the temperature of the reaction mixture was brought to 210 °C by immersing the flask into a pre-heated oil-bath (215 °C) after CO bubbling when it was stirred at 130 °C, instead of a heating mantle. The reaction was ceased by taking the flask out of the hot oil-bath after the mixture reached 210 °C and was held in air for 5 min. The NCs were washed and isolated using the same procedures.

Characterization: X-ray diffraction (XRD) patterns were collected using a PANalytical X’Pert X-ray powder diffractometer equipped with CuK α 1 radiation source ($\lambda = 0.15406$ nm). A Hitachi 7000 transmission electron microscope (TEM) operated at 75 kV was used for regular TEM imaging and a JEOL-2010 FEG TEM operated at 200kV was used for high resolution TEM imaging and energy-dispersive X-ray spectroscopy (EDS) data collection. Inductively coupled plasma optical emission spectrometric (ICP-OES) analysis was carried out on a Perkin-Elmer Optima 7000 DV, whereas inductively coupled plasma mass spectrometric (ICP-MS) analysis was performed on a Varian 810 ICP-mass spectrometer.

EDS sample preparation procedure: In order to get accurate EDS result, all of our samples have been carefully cleaned. Every TEM grid for EDS characterization was made from the sample washed several times as described below. 1.0 mL Pt-M nanoparticles synthesized through above routine in hexane was mixed well with 10.0 ml acetone and 20.0 mL methanol. After being ultrasonic for at least 5 min, the particles were isolated by centrifugation then re-

dispersed in chloroform. One drop of sample was dispersed on carbon-supported copper grid and dried out in air for EDS detection.

ICP sample preparation procedure: The cleaning steps for preparing ICP characterization samples are as same as for EDS. After the cleaning, 1.0 mL freshly made nitrohydrochloric acid was used to dissolve the precipitates. Sufficient DI water was used to dilute the acid solution to 40 mL when there was no residue in it. Each aqueous mixture was further diluted to appropriate concentration for ICP test.

Table S1. EDS* and ICP-MS/ICP-OES Analysis Results

Sample		EDS (at%)	ICP-MS (at%)	ICP-OES (at%)
Pt/M	Synthesis temperature			
Pt/Fe	200 °C	88.09/11.91	79.07/20.93	84.06/15.94
	240 °C	93.31/6.69		91.11/8.89
	210 °C oil-bath	92.93/7.07		90.28/9.72
Pt/Ni	200 °C	95.30/4.70	94.29/5.71	93.14/6.86
	240 °C	89.79/10.21		87.81/12.19
	210 °C oil-bath	91.08/8.92		89.14/10.86
Pt/Co	200 °C	94.54/5.46	94.46/5.54	95.10/4.90
	240 °C	94.14/5.86		93.38/6.62
	210 °C oil-bath	96.57/3.43		97.21/2.79

(*All data were averaged on the basis of at least three measurements on different positions)

Figure S1. Photograph of Pt-M NC suspensions in hexane. Samples were statically stored for a certain period of time after a preparation at 200 °C and growth for 5 min in the presence of CO through the “heating mantle” route. A), Pt-Fe NCs (12 hrs after the synthesis); B), Pt-Ni NCs (12 hrs after the synthesis); C), Pt-Co NCs (12 hrs after the synthesis); D), Pt-Co NCs (1 hr after the synthesis).

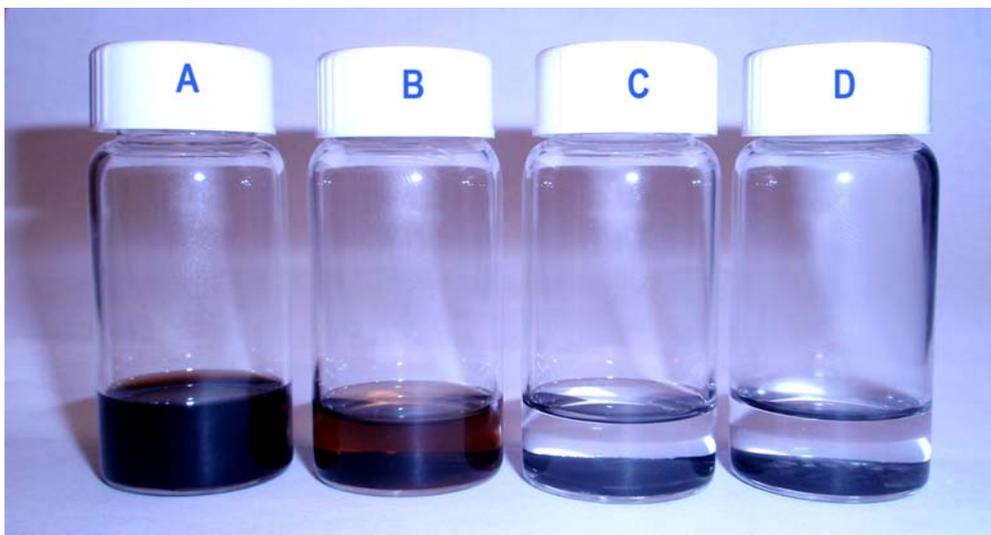
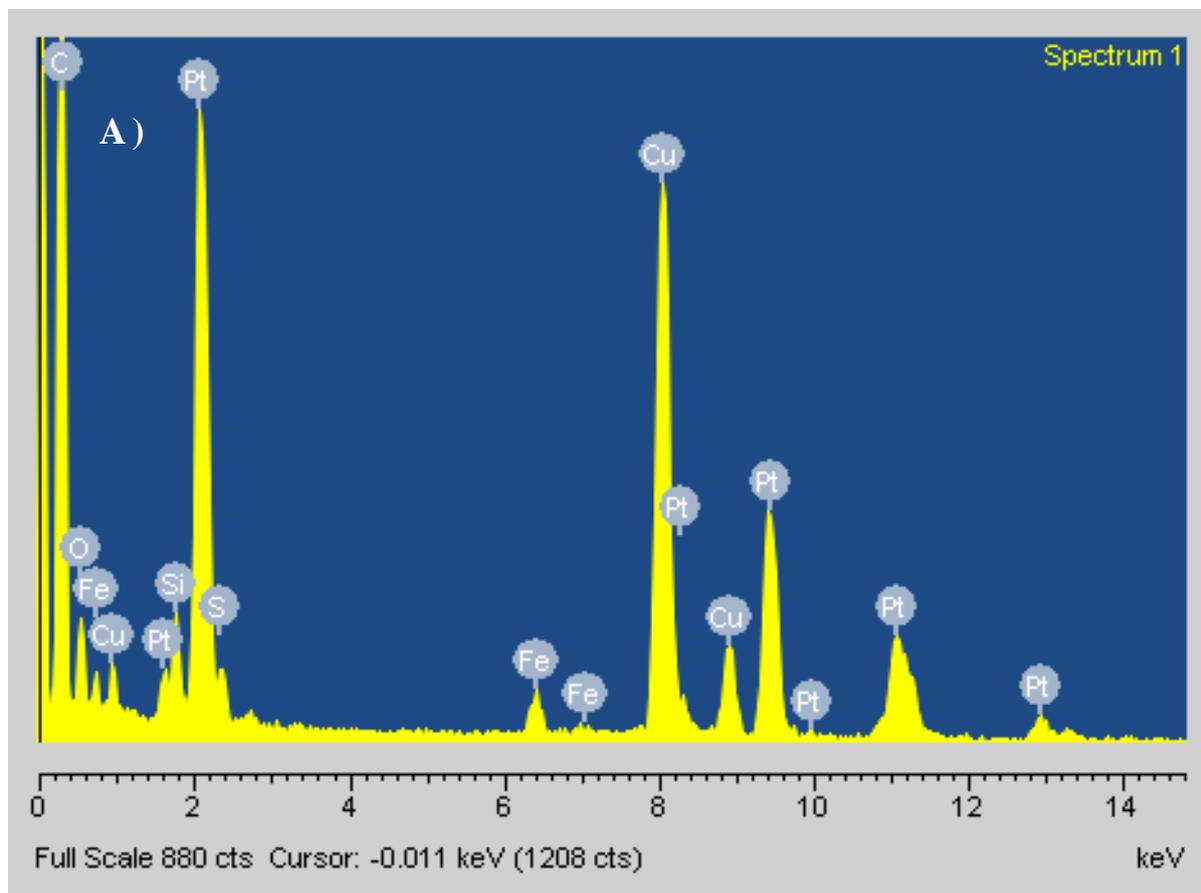


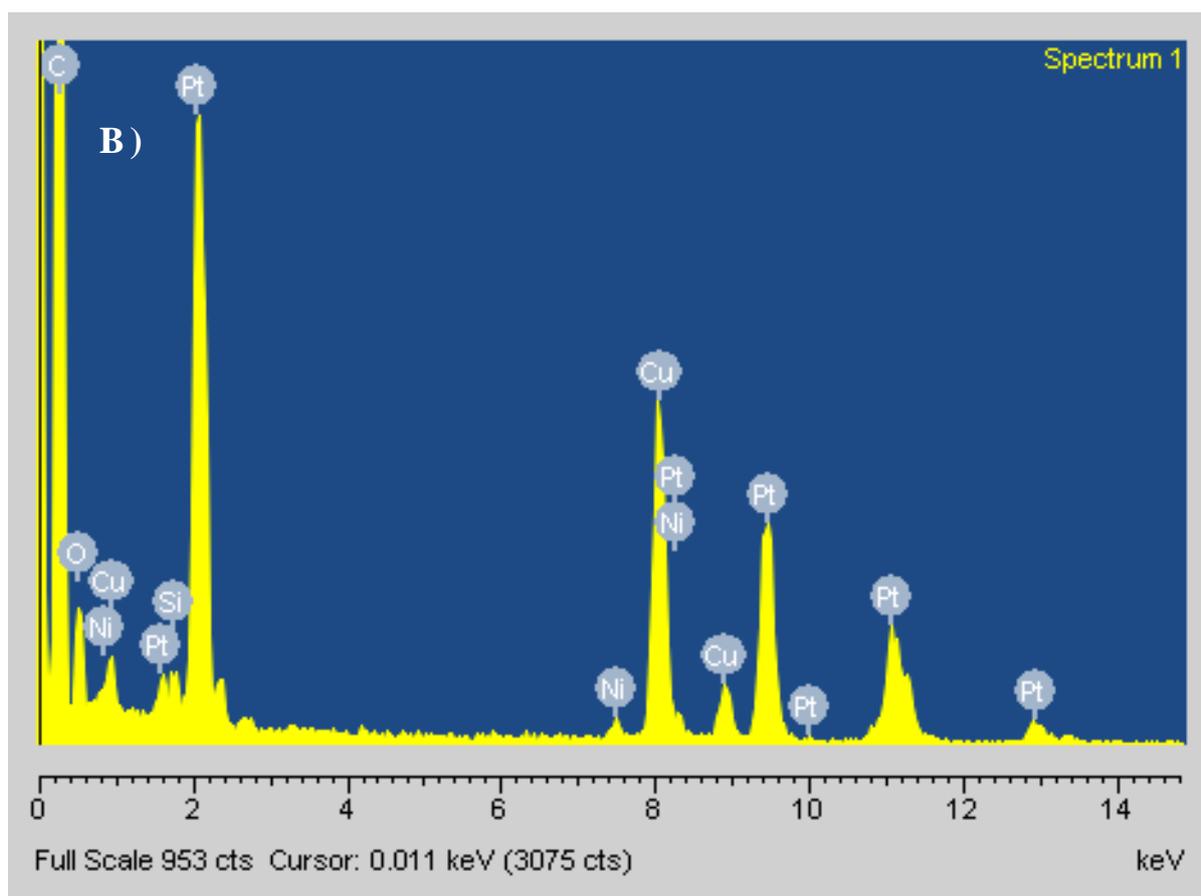
Figure S2. EDS@TEM analysis data and typical spectra of Pt-M NCs prepared at 200 °C and grew for 5 min in the presence of CO through the “heating mantle” route. A), Pt-Fe NCs; B), Pt-Ni NCs; and C), Pt-Co NCs.



Processing Option: All elements analyzed (Normalized)

All results in atomic%

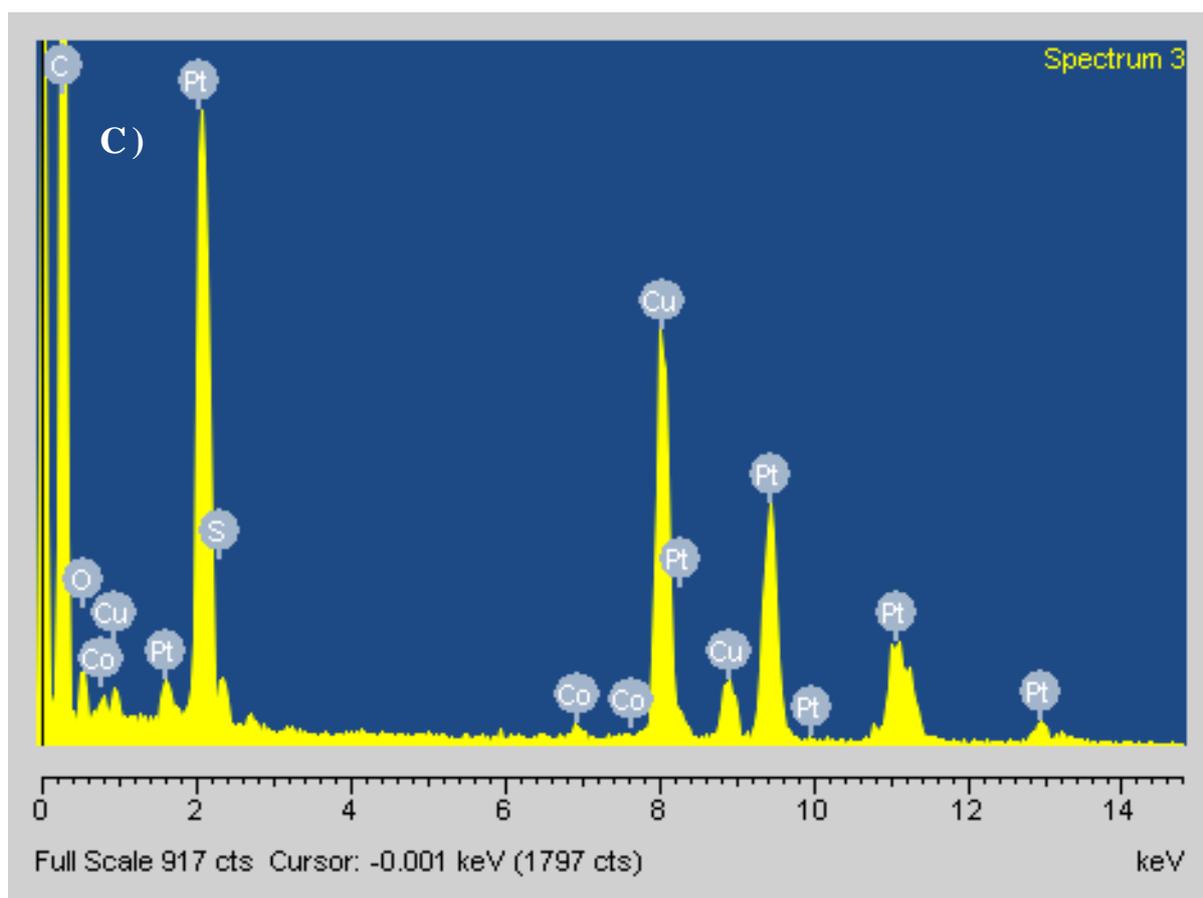
Spectrum	In stats.	Fe	Pt
<u>Spectrum 1</u>	Yes	12.88	87.12
Spectrum 2	Yes	12.00	88.00
Spectrum 3	Yes	10.85	89.15
Mean		11.91	88.09
Std. deviation		1.02	1.02
Max.		12.88	89.15
Min.		10.85	87.12



Processing Option: All elements analyzed (Normalized)

All results in atomic%

Spectrum	In stats.	Ni	Pt
<u>Spectrum 1</u>	Yes	5.20	94.80
Spectrum 2	Yes	5.53	94.47
Spectrum 3	Yes	3.38	96.62
Mean		4.70	95.30
Std. deviation		1.16	1.16
Max.		5.53	96.62
Min.		3.38	94.47



Processing Option: All elements analyzed (Normalized)

All results in atomic%

Spectrum	In stats.	Co	Pt
Spectrum 1	Yes	3.90	96.10
Spectrum 2	Yes	6.10	93.90
<u>Spectrum 3</u>	Yes	5.65	94.35
Spectrum 4	Yes	6.20	93.80
Mean		5.46	94.54
Std. deviation		1.07	1.07
Max.		6.20	96.10
Min.		3.90	93.80

Figure S3. XRD patterns of Pt and Pt-M alloy nanocrystals. Samples were prepared at 200 °C in the presence of CO through the “heating mantle” route and were measured on a standard XRD holder.

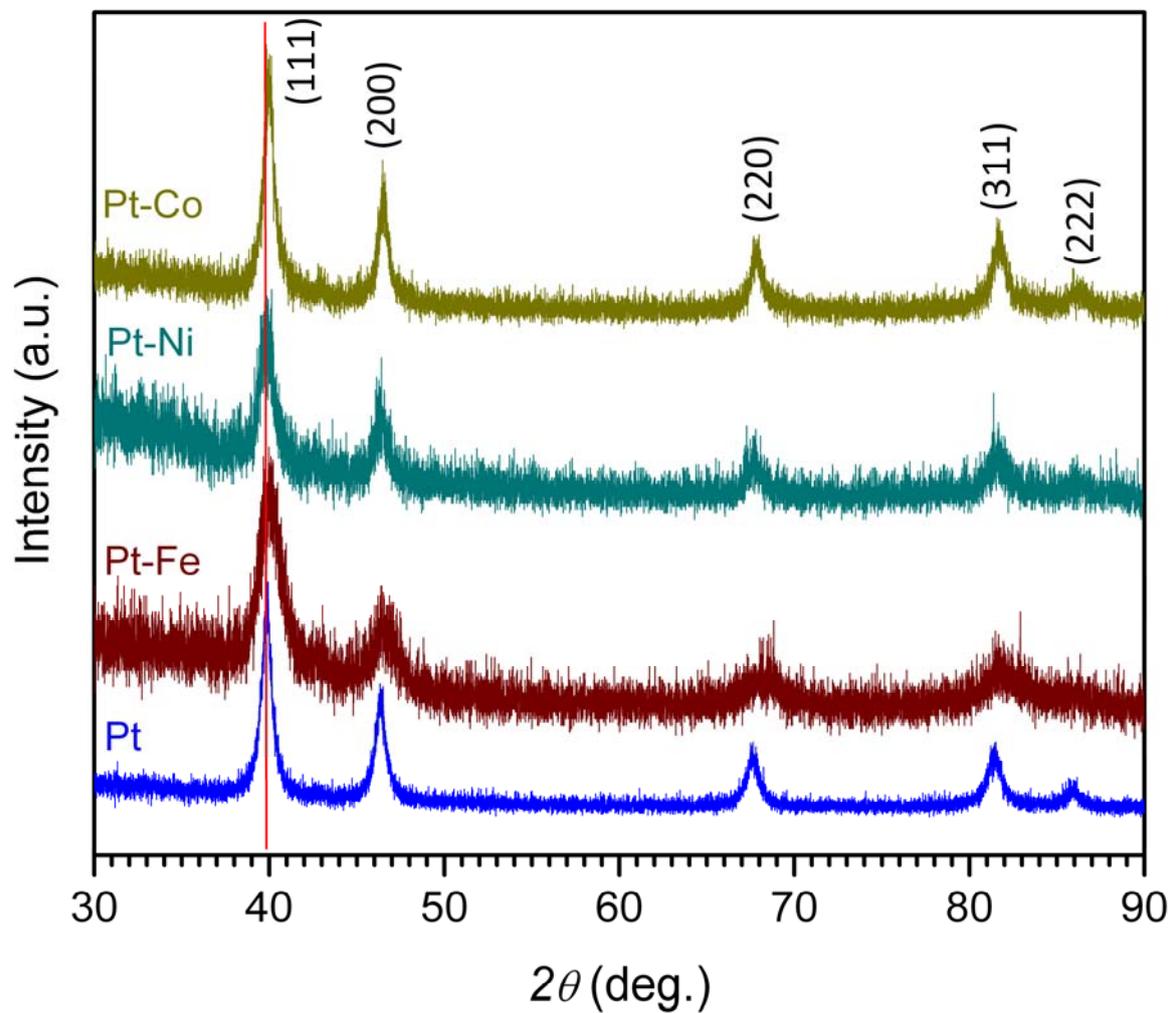
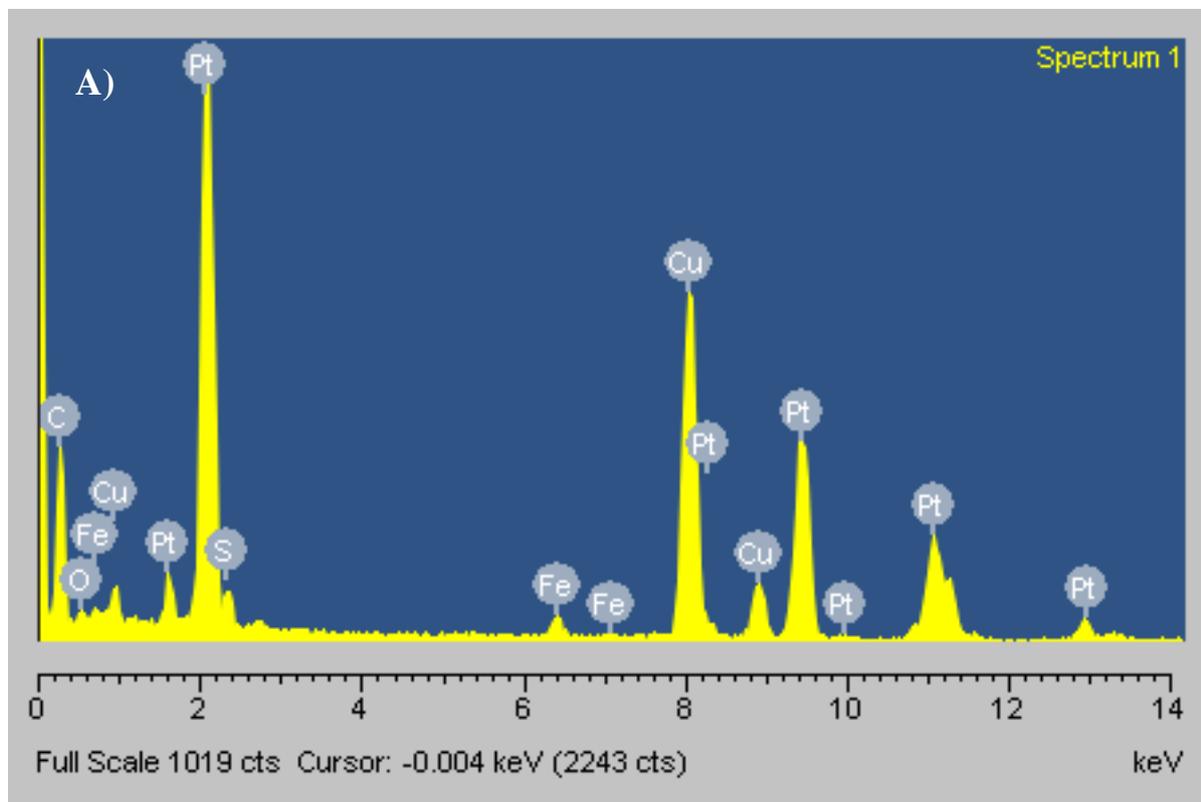


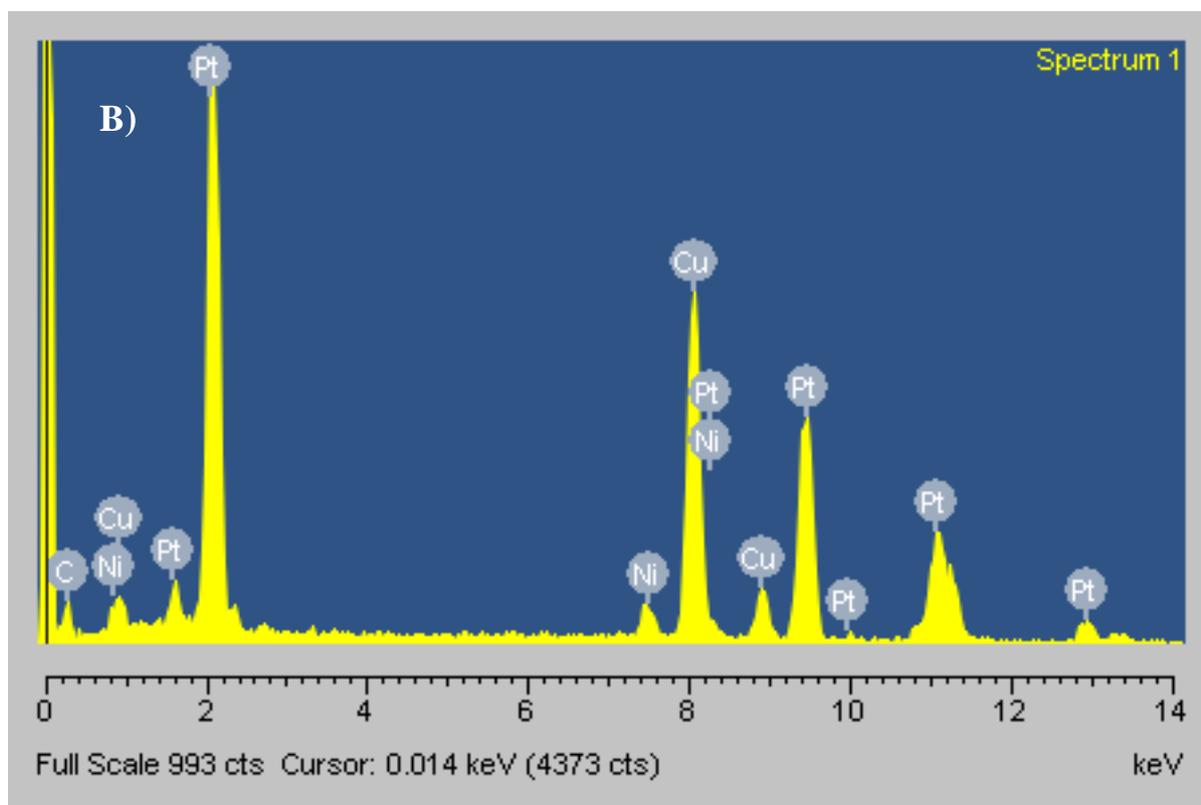
Figure S4. EDS@TEM analysis data and typical spectra of Pt-M NCs prepared at 240 °C and grew for 5 min in the presence of CO through the “heating mantle” route. A), Pt-Fe NCs; B), Pt-Ni NCs; and C), Pt-Co NCs.



Processing option: All elements analyzed (Normalized)

All results in atomic%

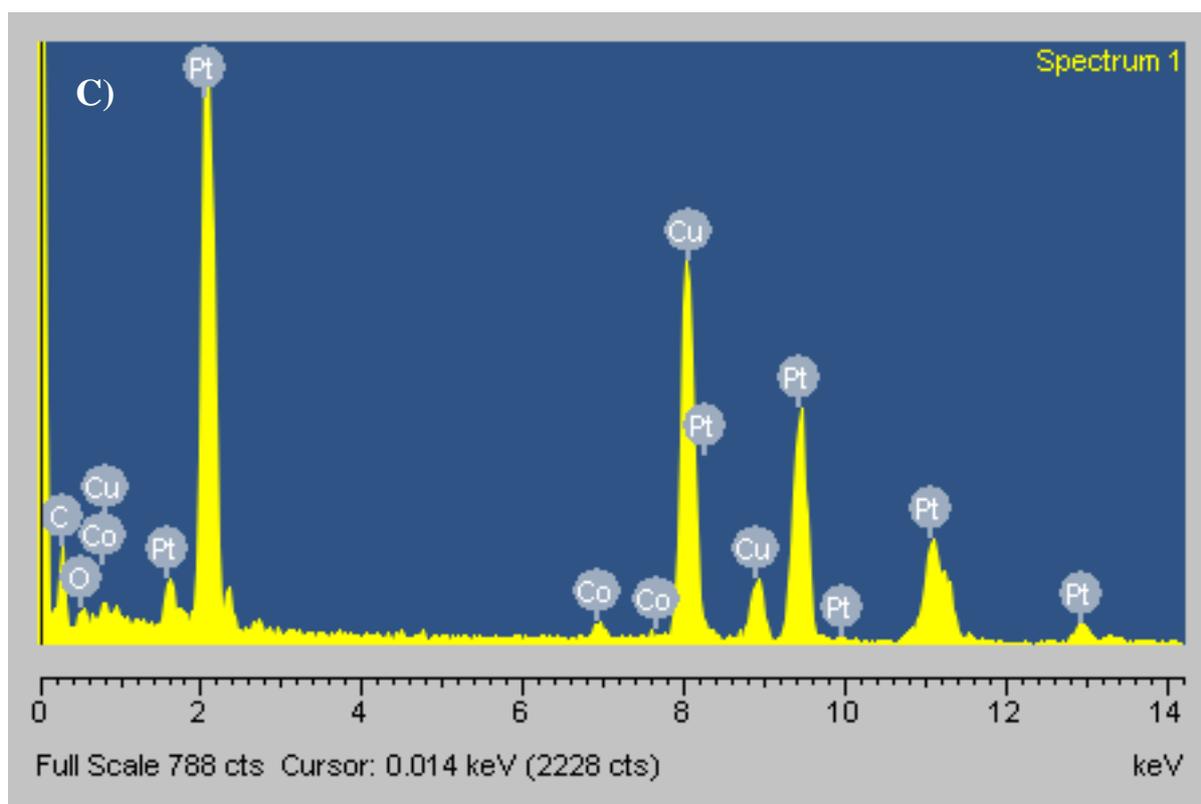
Spectrum	In stats.	Fe	Pt
<i>Spectrum 1</i>	Yes	6.84	93.16
Spectrum 2	Yes	6.23	93.77
Spectrum 3	Yes	6.34	93.66
Spectrum 4	Yes	7.05	92.95
Spectrum 5	Yes	7.00	93.00
Mean		6.69	93.31
Std. deviation		0.38	0.38
Max.		7.05	93.77
Min.		6.23	92.95



Processing option: All elements analyzed (Normalized)

All results in atomic%

Spectrum	In stats.	Ni	Pt
<u>Spectrum 1</u>	Yes	10.31	89.69
Spectrum 2	Yes	10.46	89.54
Spectrum 3	Yes	9.28	90.72
Spectrum 4	Yes	9.99	90.01
Spectrum 5	Yes	11.03	88.97
Mean		10.21	89.79
Std. deviation		0.64	0.64
Max.		11.03	90.72
Min.		9.28	88.97



Processing option: All elements analyzed (Normalized)

All results in atomic%

Spectrum	In stats.	Co	Pt
<u>Spectrum 1</u>	Yes	5.61	94.39
Spectrum 2	Yes	33.60	66.40 (discarded)
Spectrum 3	Yes	5.53	94.47
Spectrum 4	Yes	5.47	94.53
Spectrum 5	Yes	6.84	93.16
Mean		5.86	94.14
Std. deviation		0.83	0.33
Max.		6.84	94.53
Min.		5.47	93.16

Figure S5. XRD patterns of Pt and Pt-M alloy nanocrystals. Samples were prepared at 240 °C in the presence of CO through the “heating mantle” route and were measured on a standard XRD holder.

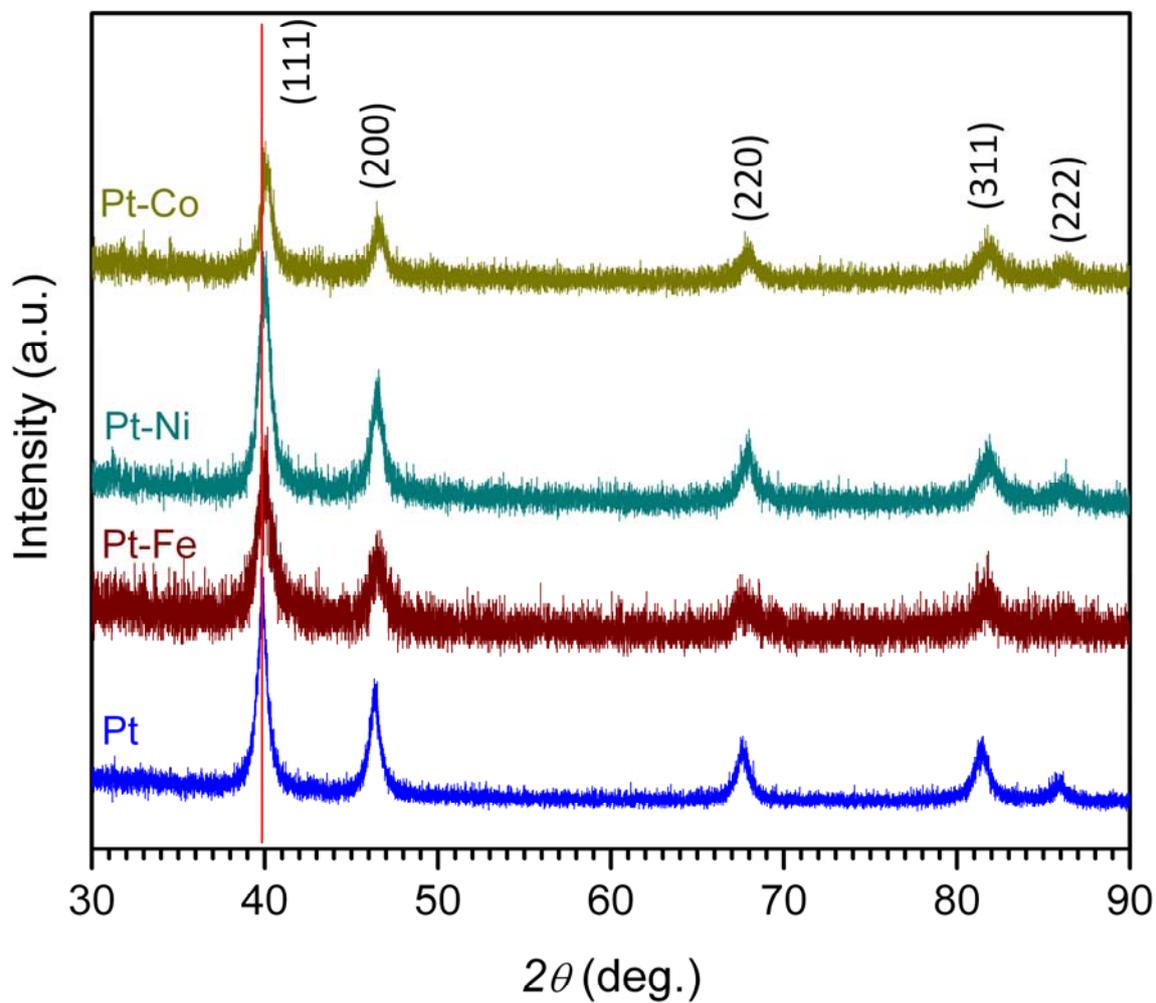
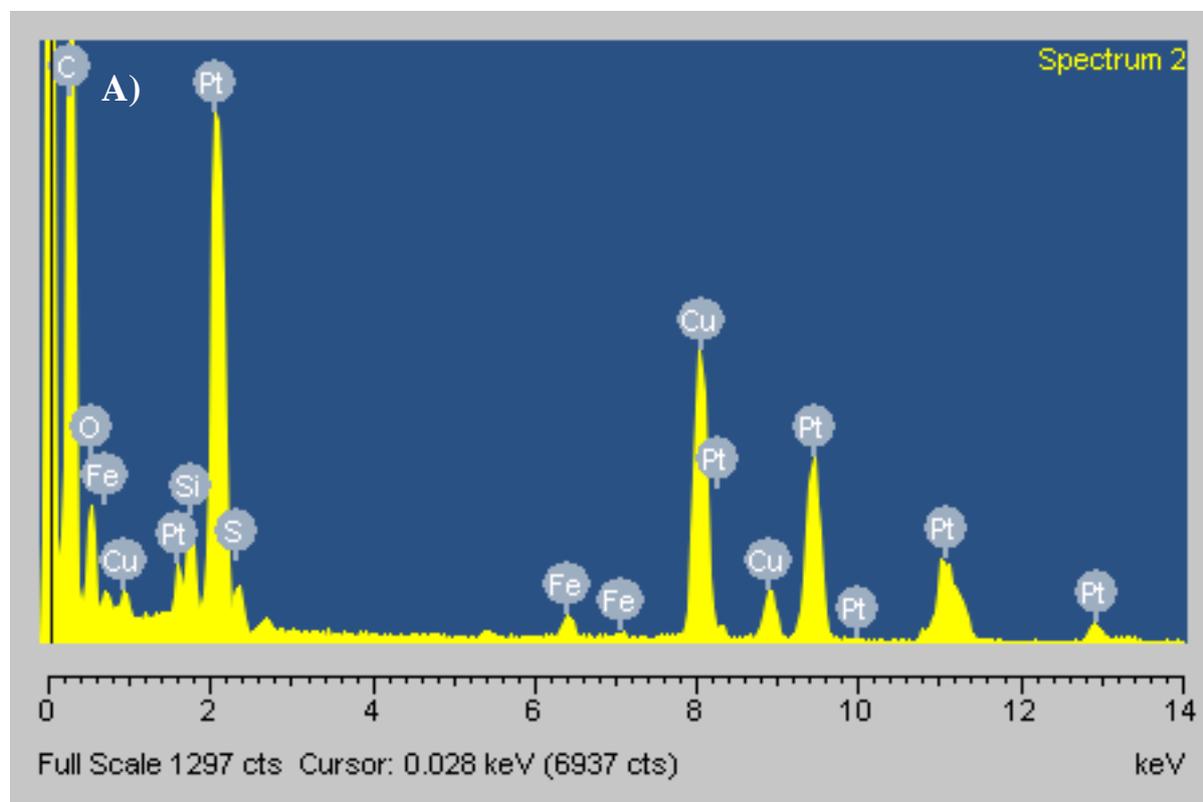


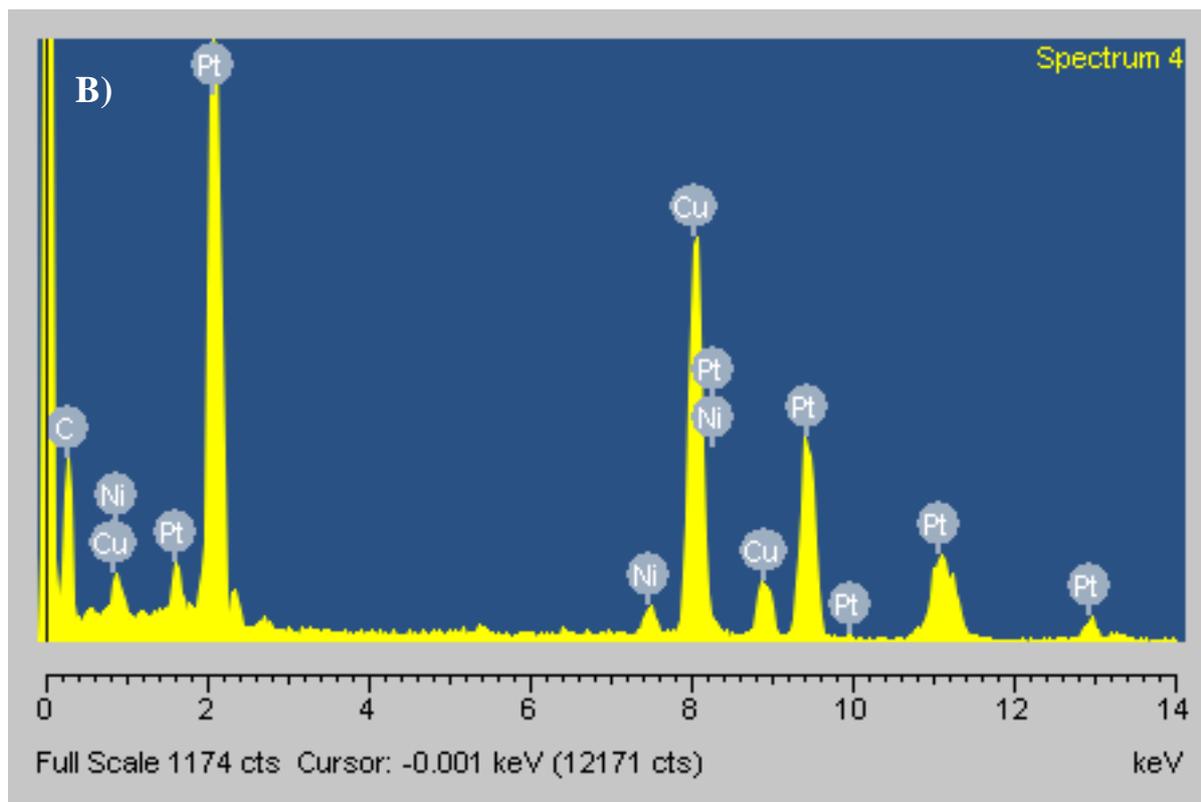
Figure S6. EDS@TEM analysis data and typical spectra of Pt-M NCs prepared using a high-temperature oil-bath at 210 °C and grew for 5 min through the “hot oil-bath” route. A), Pt-Fe NCs; B), Pt-Ni NCs; and C), Pt-Co NCs.



Processing option: All elements analyzed (Normalized)

All results in atomic%

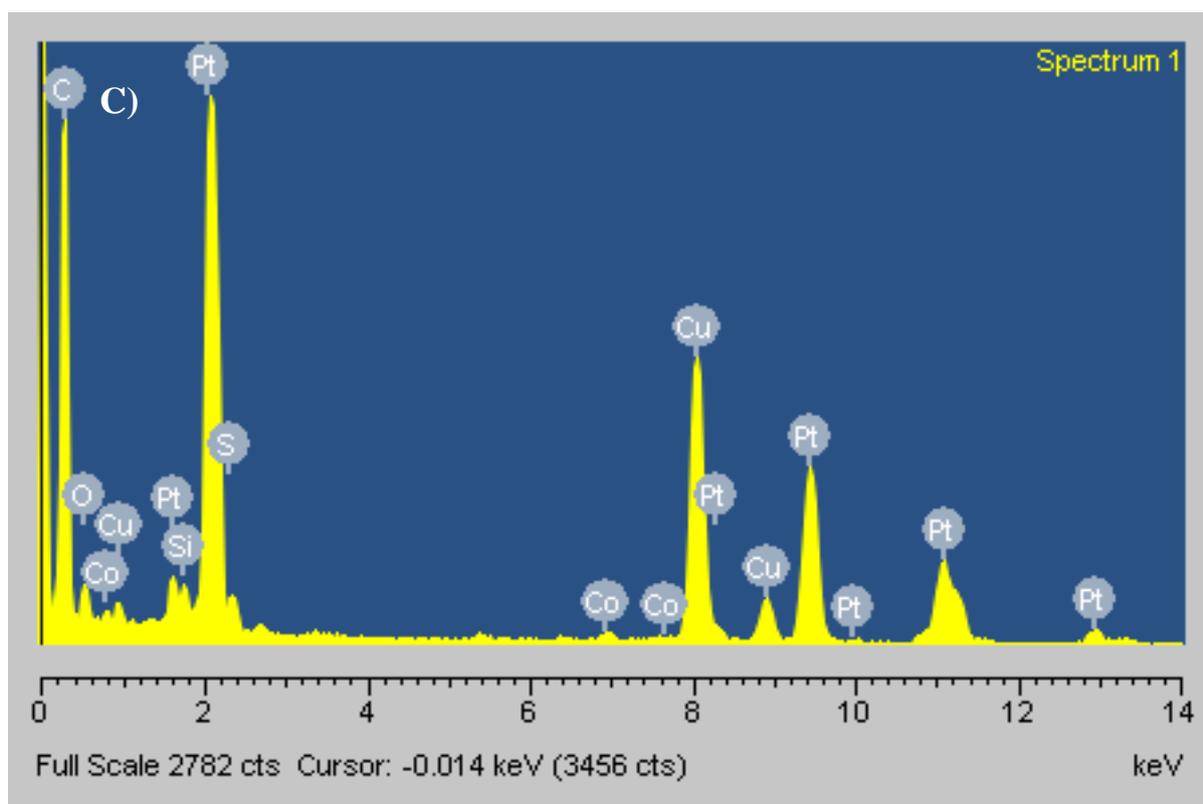
Spectrum	In stats.	Fe	Pt
Spectrum 1	Yes	5.90	94.10
<u>Spectrum 2</u>	Yes	9.13	90.87
Spectrum 3	Yes	6.86	93.14
Spectrum 4	Yes	7.58	92.42
Spectrum 5	Yes	5.89	94.11
Mean		7.07	92.93
Std. deviation		1.35	1.35
Max.		9.13	94.11
Min.		5.89	90.87



Processing option: All elements analyzed (Normalized)

All results in atomic%

Spectrum	In stats.	Ni	Pt
Spectrum 1	Yes	9.04	90.96
Spectrum 2	Yes	9.48	90.52
Spectrum 3	Yes	8.33	91.67
<u>Spectrum 4</u>	Yes	8.84	91.16
Spectrum 5	Yes	8.90	91.10
Mean		8.92	91.08
Std. deviation		0.41	0.41
Max.		9.48	91.67
Min.		8.33	90.52



Processing option: All elements analyzed (Normalized)

All results in atomic%

Spectrum	In stats.	Co	Pt
<u>Spectrum 1</u>	Yes	3.82	96.18
Spectrum 2	Yes	3.55	96.45
Spectrum 3	Yes	2.95	97.05
Spectrum 4	Yes	3.53	96.47
Spectrum 5	Yes	3.28	96.72
Mean		3.43	96.57
Std. deviation		0.33	0.33
Max.		3.82	97.05
Min.		2.95	96.18

Figure S7. XRD patterns of Pt and Pt-M alloy nanocrystals. Samples were prepared in a hot oil-bath at 210 °C and were measured on a standard XRD holder.

