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Electronic Supplementary Information (ESI)

Colloidal nickel/gallium nanoalloys obtained from organometallic precursors in conventional organic solvents and in ionic liquids: Noble-metal-free alkyne semihydrogenation catalysts.

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Ni-Ga phase diagrams

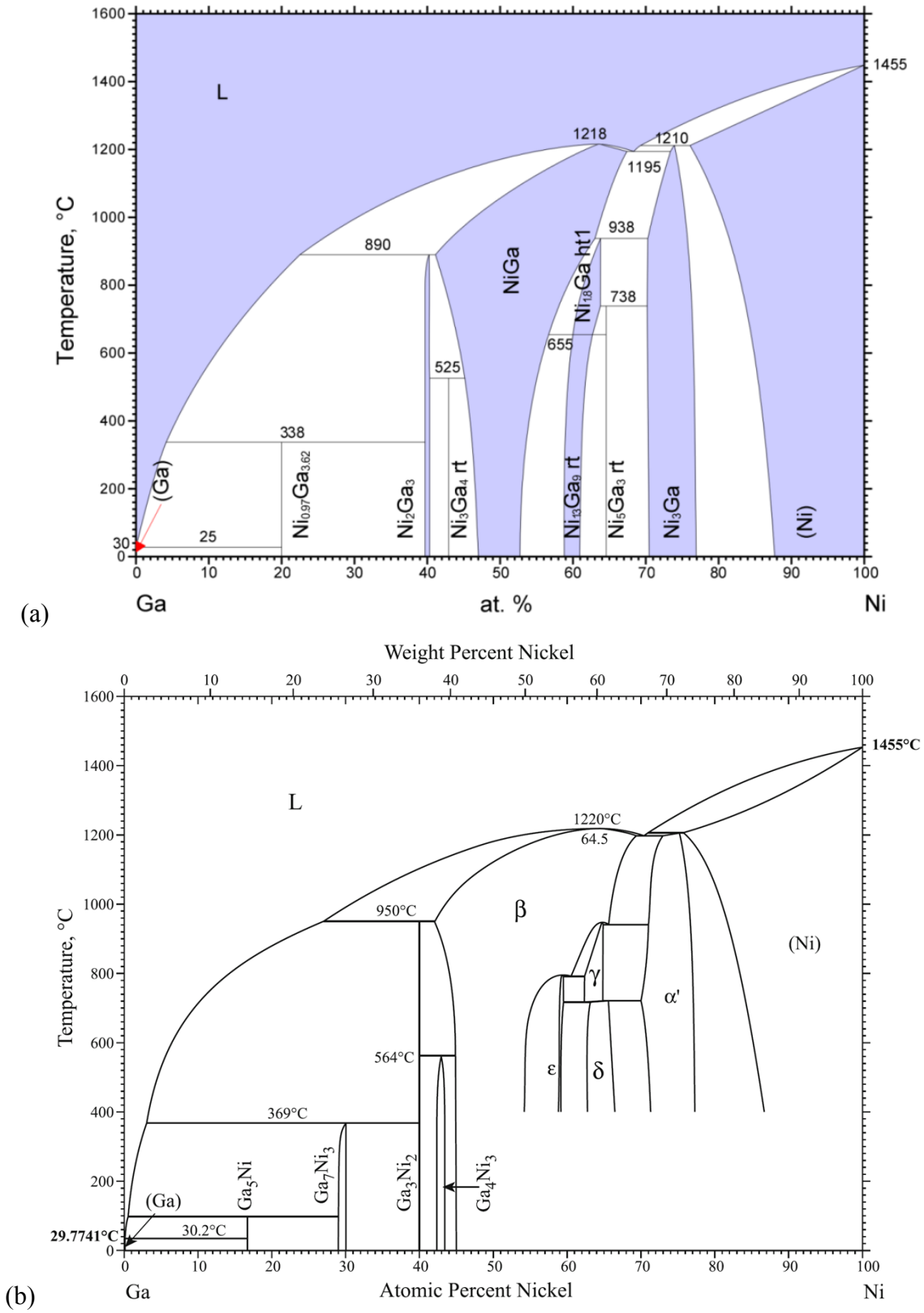


Figure S1a Nickel-Gallium binary alloy phase diagrams. (a) from ref. [1], (b) from ref. [2]

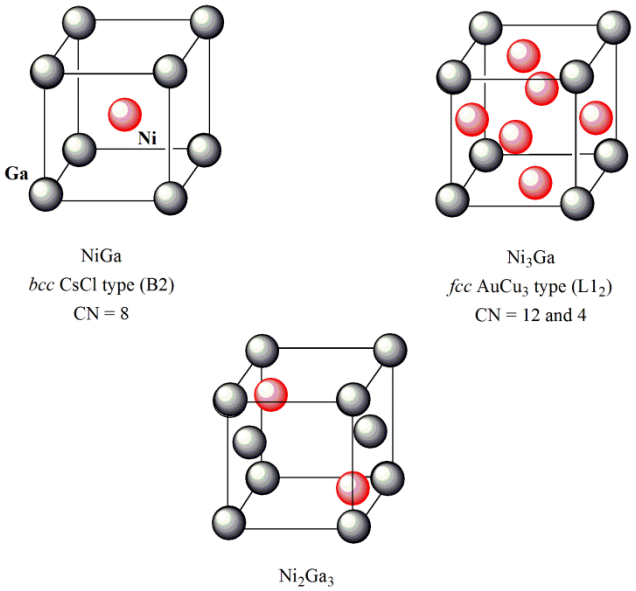


Figure S1b Schematic illustration of selected Ni-Ga intermetallic phases (cf Fig. S1).

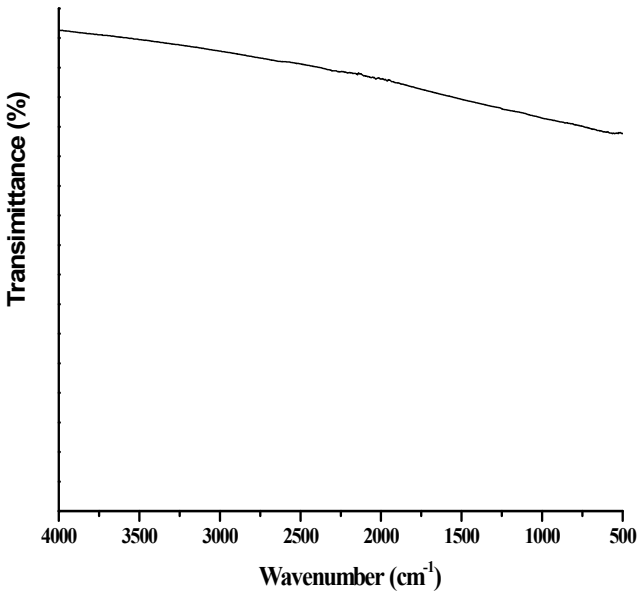


Figure S2 Infrared spectrum of the black material (**NP1**). The sample was measured as neat.

EDX of NP1 – NP3

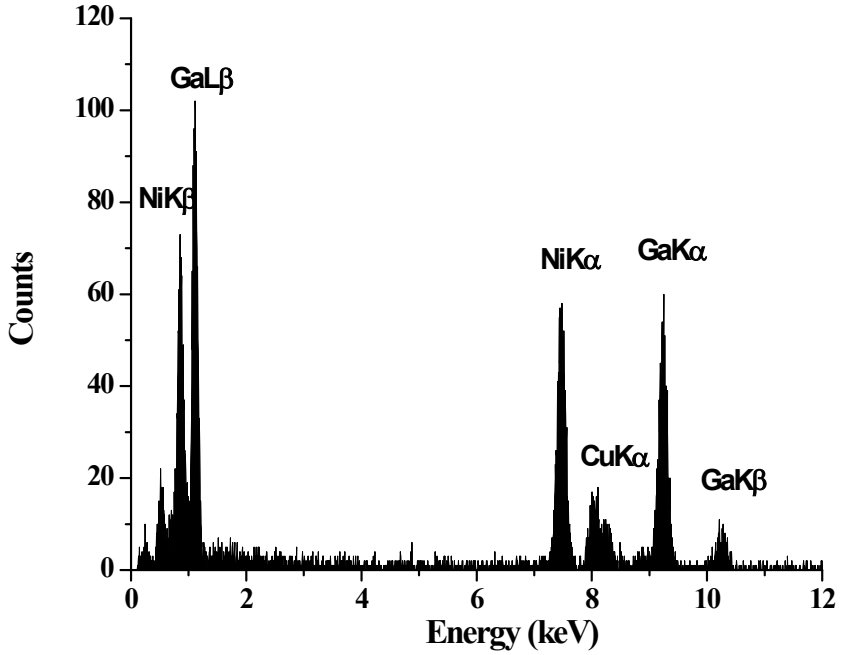


Figure S3 Energy dispersive X-ray (EDX) spectrum of the sample **NP1**

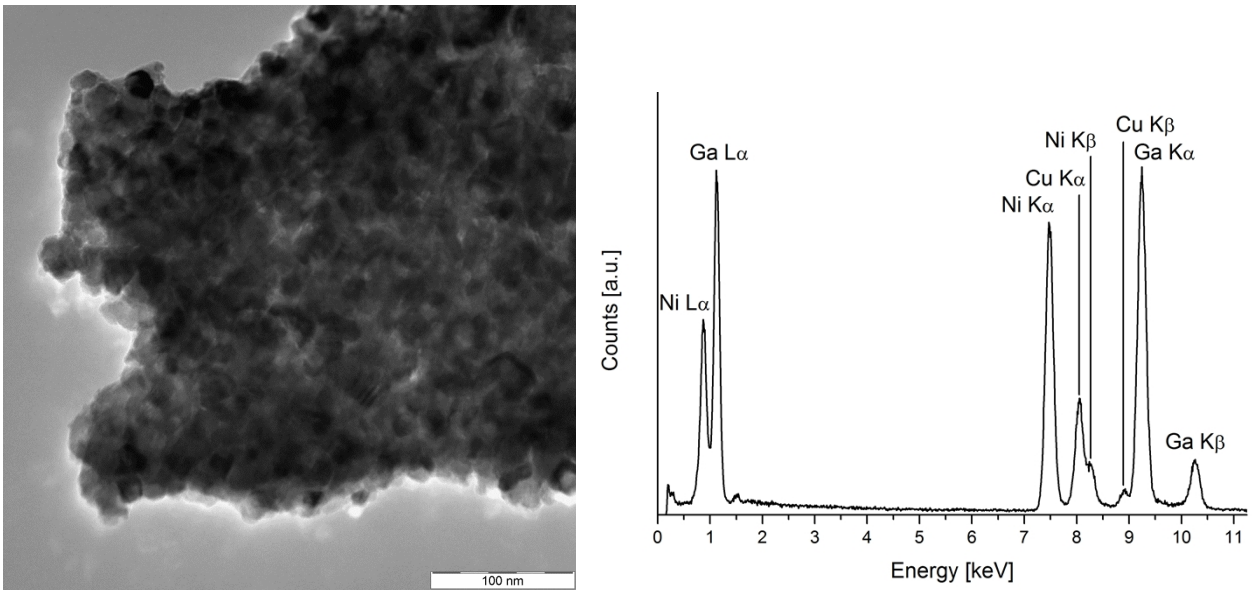


Figure S4 BF-TEM and EDX of the material **NP2** obtained according to Scheme 2.

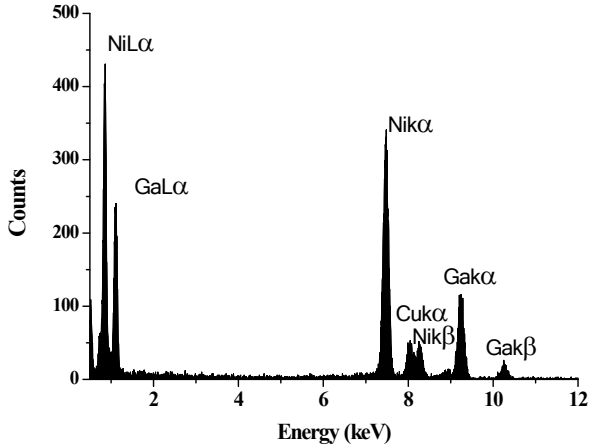


Figure S5 Energy dispersive X-ray (EDX) spectrum of the sample **NP3**.

Table S1 Ratios of Ni to Ga of different Ni_xGa_y agglomerates in the samples **NP1**, **NP2**, and **NP3**. The first row shows the ratio of the desired phases NiGa, Ni_2Ga_3, and Ni_3Ga. The ratios have been calculated from quantified EDX spectra.

	NP1			**NP2**			**NP3**		
	Ni	:	Ga	Ni	:	Ga	Ni	:	Ga
desired ratio	**1**		**1**	**1**		**1.5**	**1**		**0.33**
	1		1.06	1		1.13	1		0.42
	1		1.01	1		1.86	1		0.28
	1		1.11	1		2.13	1		0.33
	1		0.99	1		1.60	1		0.39
				1		1.13	1		0.28
				1		1.86	1		0.31

Thermogravimetric analysis of [Ni(GaCp*)(PMe$_3$)$_3$] (used as a single-source precursor for **NP4** and **NP8**) **and TGA of [Ni(GaCp*)$_3$(PCy$_3$)]**

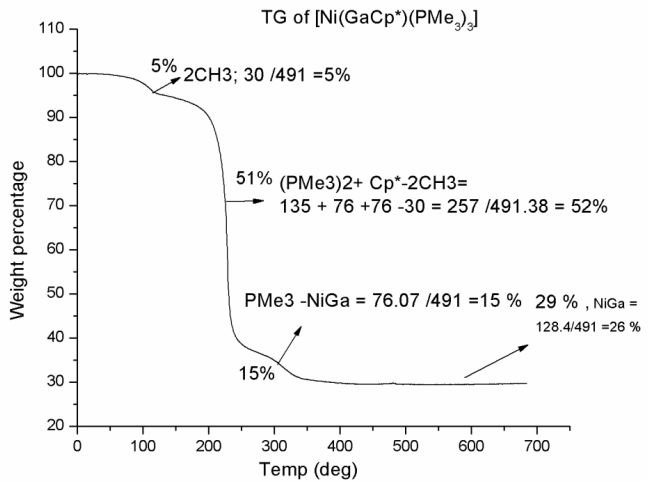


Figure S6A Thermogravimetric analysis of the single source precursor [Ni(GaCp*)(PMe$_3$)$_3$].

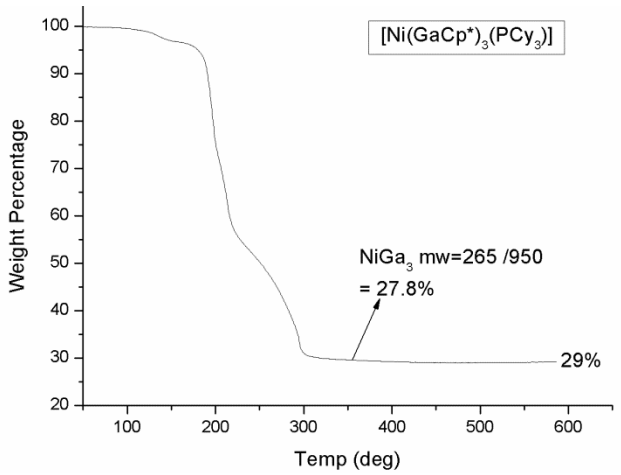


Figure S6B Thermogravimetric analysis of the single source precursor [Ni(GaCp*)$_3$(PCy$_3$)].

IR, TEM and EDX of NP4

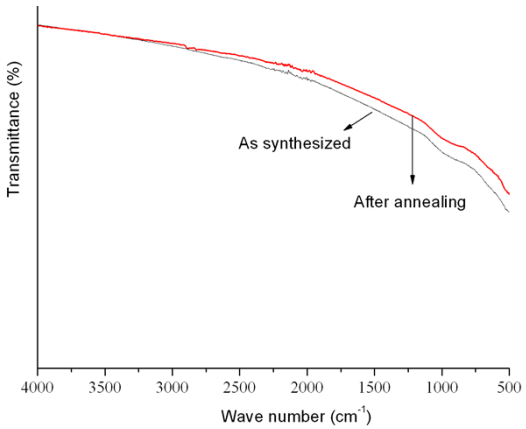


Figure S7 IR of the sample **NP4** measured as neat before and after annealing.

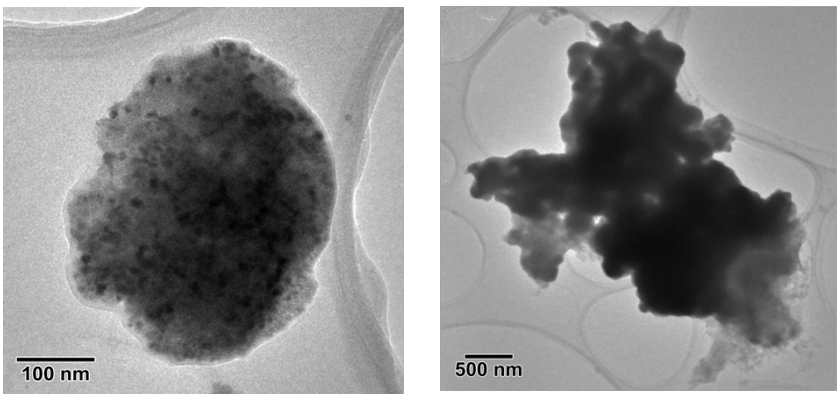


Figure S8 TEM images of the material **NP4**. Left: BF-TEM of small agglomerated particles. Right BF-TEM of large agglomerated particles. The particles are encased in an unidentified matrix. **Note**: The particles exhibit no preferred size. The BF-TEM images show smaller particles (5-20 nm) as well as the huge agglomerates (several hundred nanometers). The EDX measurement indicates the presence of multiple intermetallic phases with varying Ni to Ga ratios. To acquire EDX spectra, whole particle agglomerations were illuminated, thus the calculated elemental compositions only reveal the average composition of an agglomeration, not necessarily of the individual particles. The EDX analysis was performed on several such agglomerations on the grid. The found ratios of Ni to Ga were approximately 1:1, 2:3 and 1:2 (within the accuracy of the method of measurement), means the material obtained is not completely phase pure, with only Ni_2Ga_3 as the crystalline phase as it is supported by the powder X-ray diffraction data.

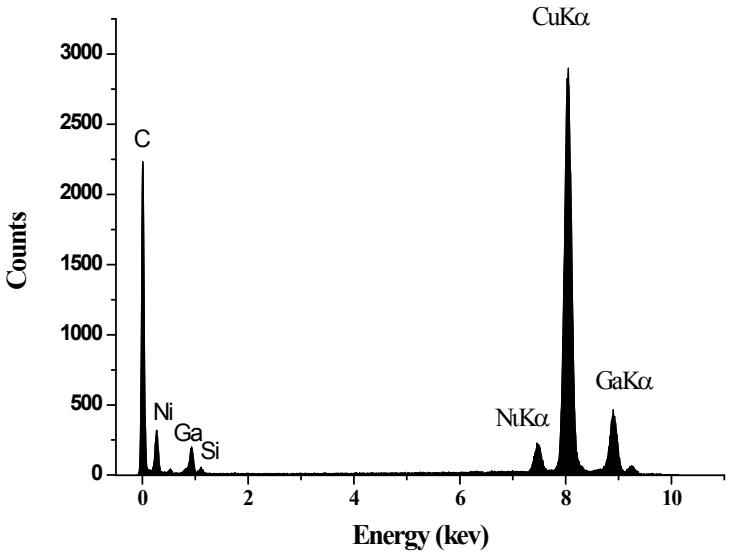


Figure S9 Energy dispersive X-ray (EDX) spectrum of the sample **NP4**.

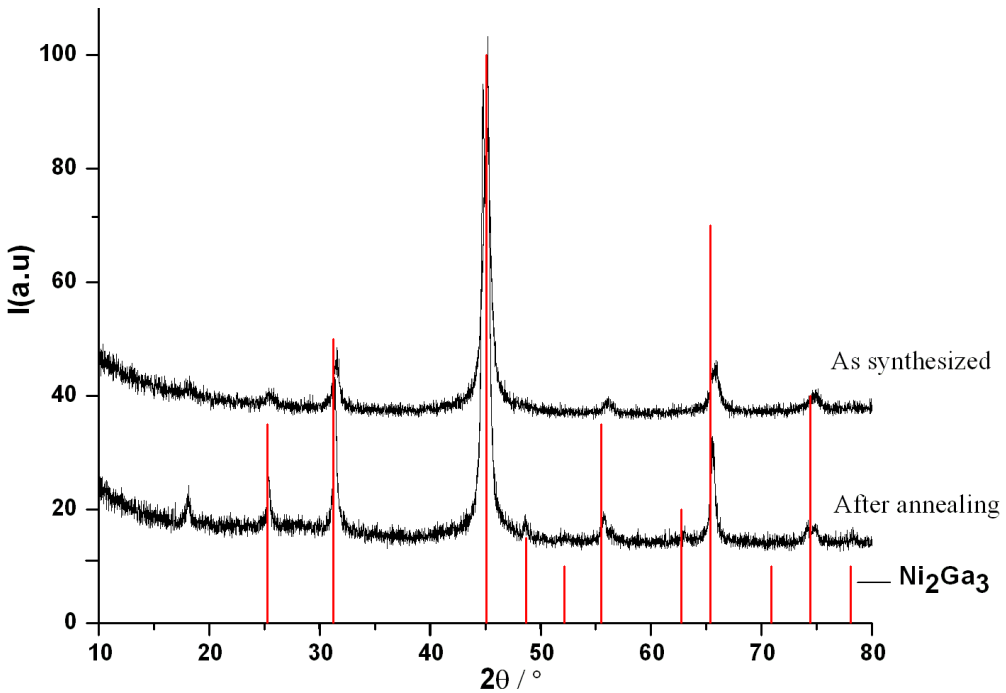
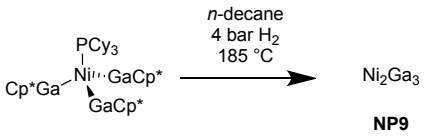


Figure S10 PXRD of Ni_2Ga_3 particles **NP4**.

Decomposition of [Ni(GaCp*)$_3$(PCy$_3$)] (NP9) incl. PXRD, TEM and EDX characterization



Scheme S1 Hydrogenolysis of [Ni(GaCp*)$_3$(PCy$_3$)] leading to Ni_2Ga_3 (**NP9**).

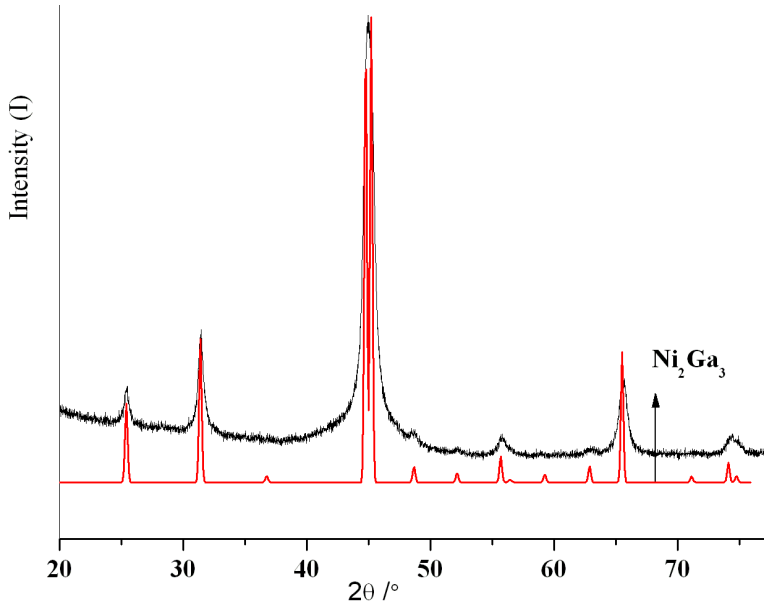
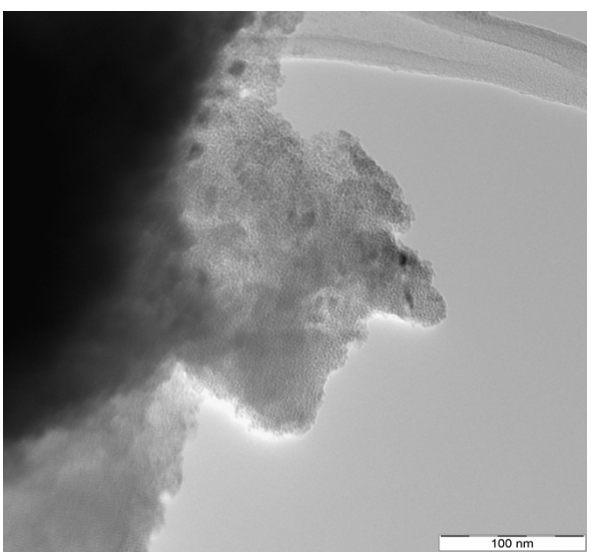
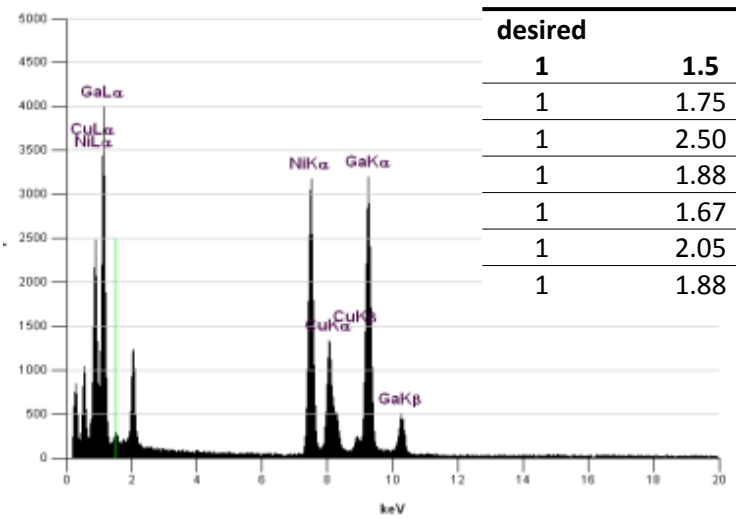


Figure S11 X-ray powder pattern for the material **NP9**. Reference data taken from ICSD: 103860. AAS analysis of the material **NP9** showed the atomic weight percentages for Ni 31.31 wt. % and Ga 52.14 wt. % which corresponds to $Ni_2Ga_{2.81}$





NP9		
Ni	:	Ga
desired		
1		**1.5**
1		1.75
1		2.50
1		1.88
1		1.67
1		2.05
1		1.88

Figure S12 BF-TEM image (left) and EDX (right) of material **NP9**.
The BF-TEM image of the dispersed powder in toluene shows the agglomerated nanoparticles as in the case of **NP2** (Fig. 1). The EDX analysis of **NP9** on few selected areas shows the presence of Ni and Ga in different ratios including the expected 2:3 phase which is the crystalline phase indicated by PXRD (Fig. S11).

EDX of NP5-NP8, XPS of NP5 and NP7 and Table of Ni:Ga ratios

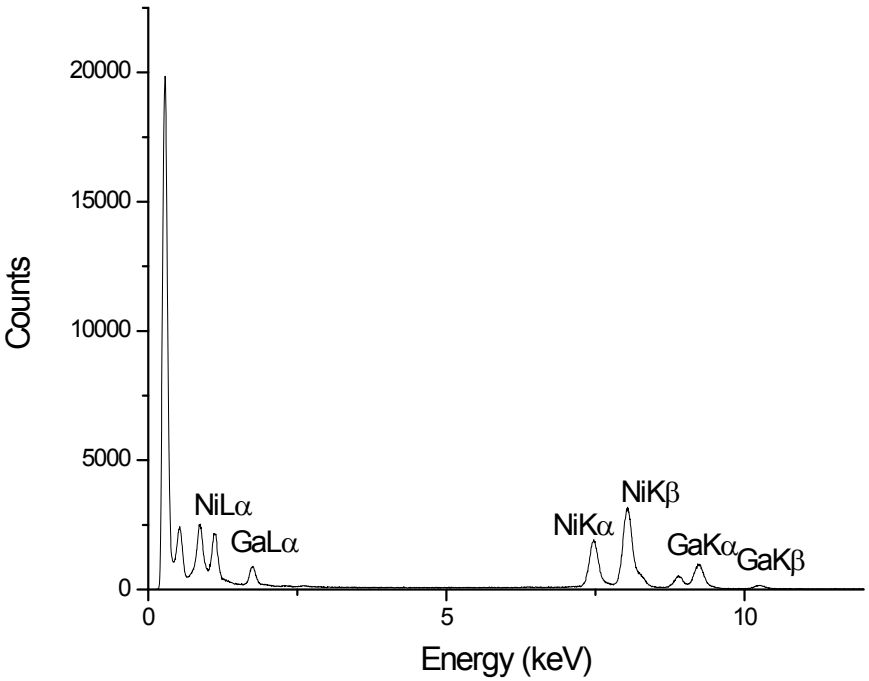


Figure S13a Energy dispersive X-ray (EDX) spectrum of the sample **NP5**.

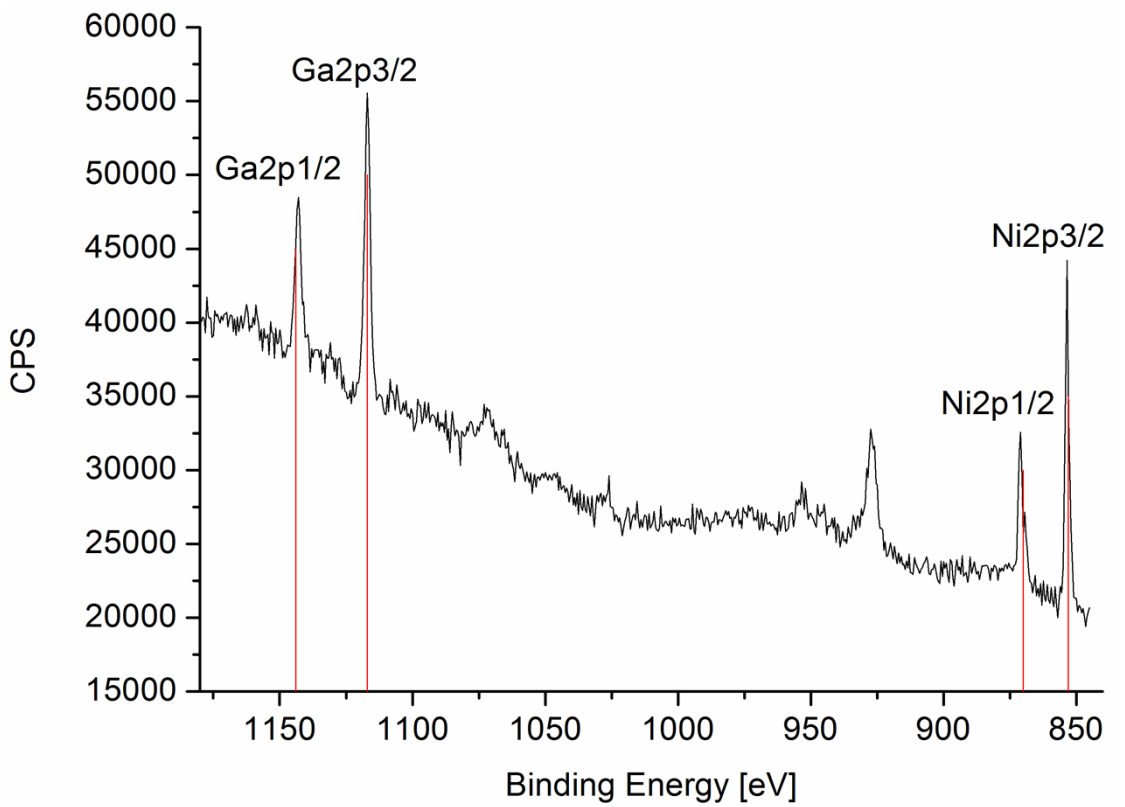


Figure S13b X-ray photoelectron, XPS-spectrum of the metal part of sample **NP5**; XPS of 50-150 mg sample in an area of 0.1 cm^2.

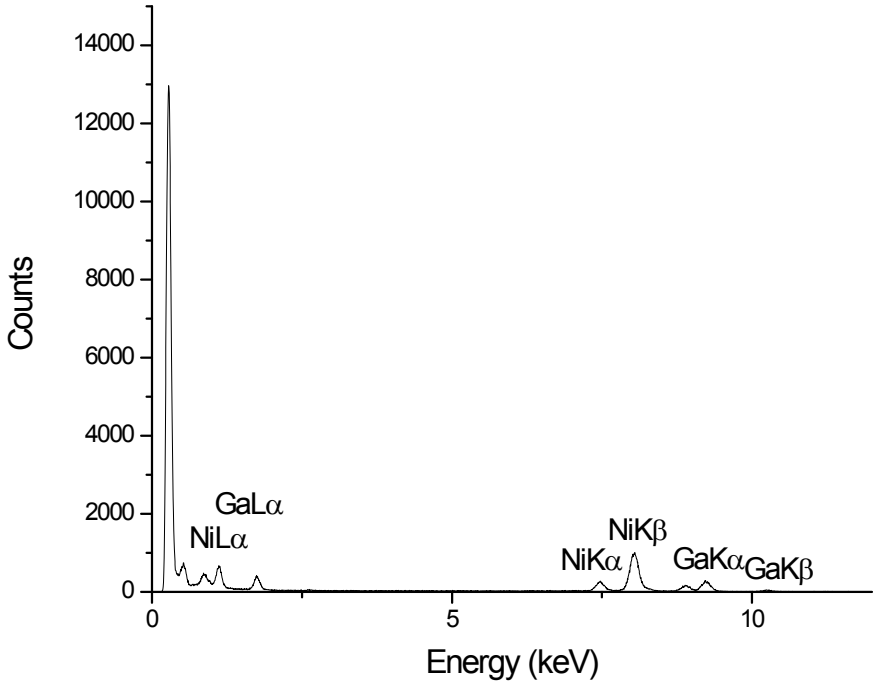


Figure S14 Energy dispersive X-ray (EDX) spectrum of the sample **NP6**.

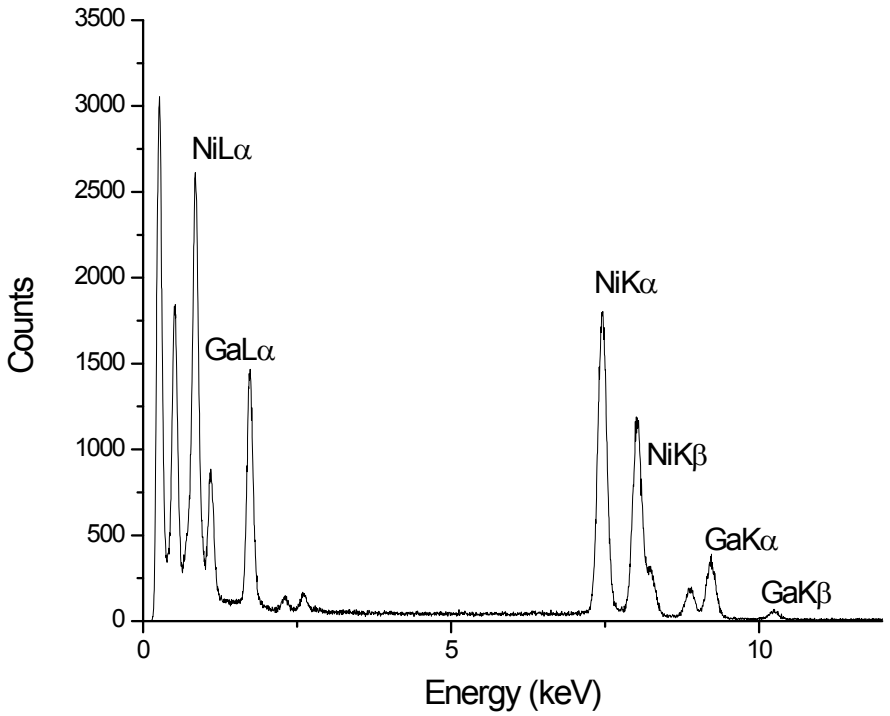


Figure S15a Energy dispersive X-ray (EDX) spectrum of the sample **NP7**.

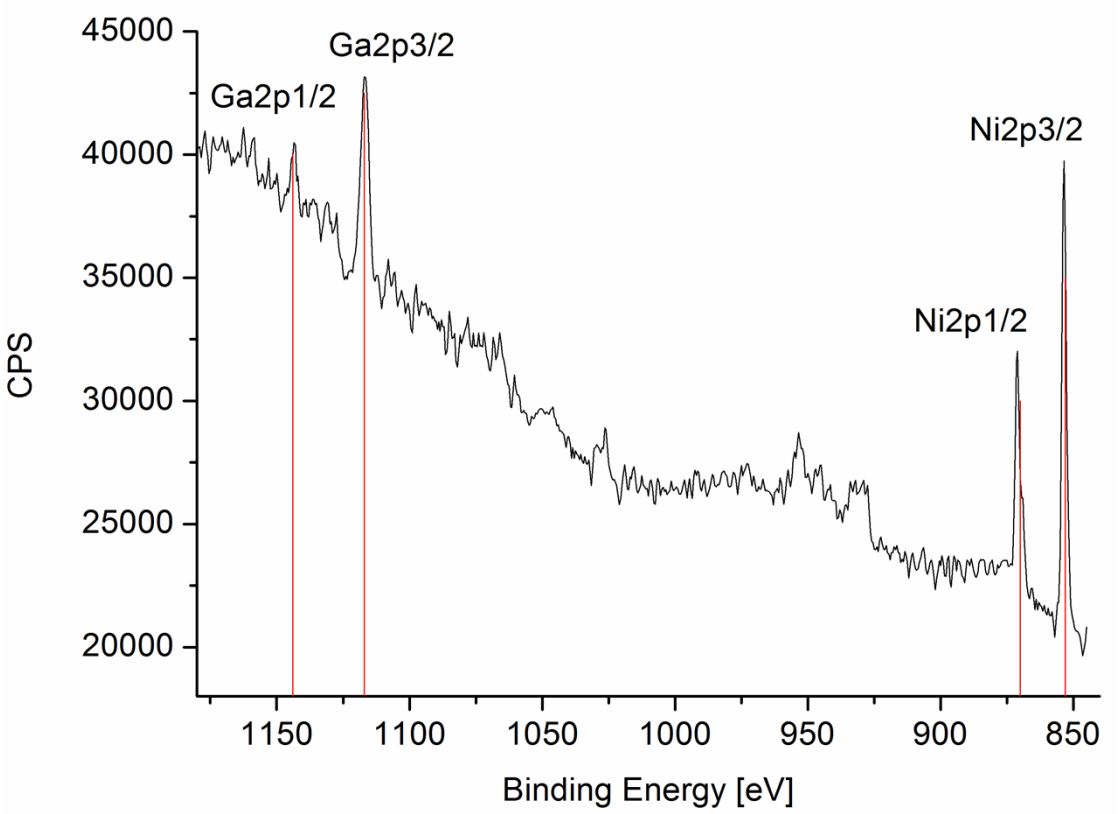


Figure S15b X-ray photoelectron, XPS-spectrum of the metal part of sample **NP7**; XPS of 50-150 mg sample in an area of 0.1 cm^2.

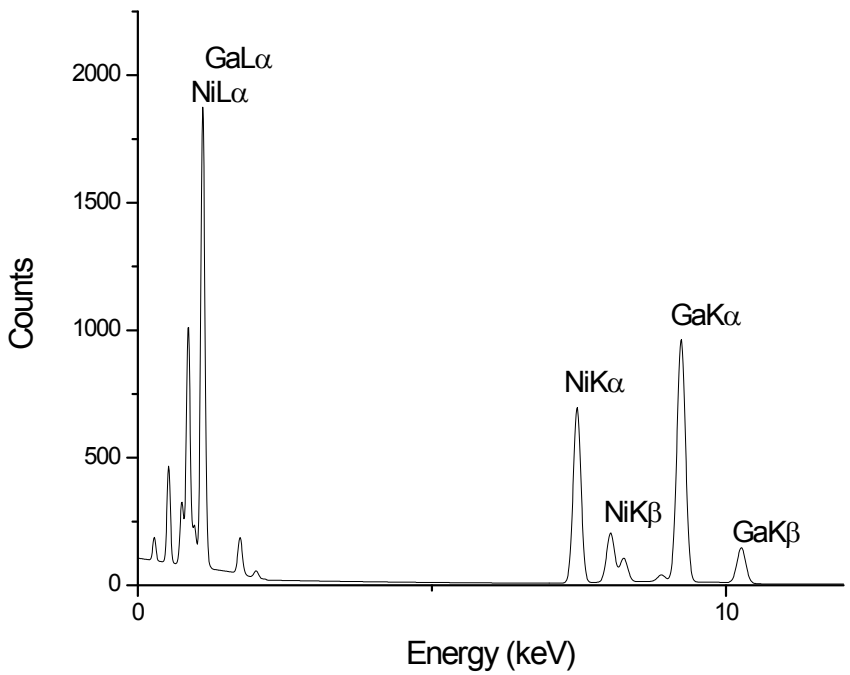


Figure S16 Energy dispersive X-ray (EDX) spectrum of the sample **NP8**.

Table S2 Ratios of Ni to Ga of different Ni_xGa_y agglomerates in the samples **NP5-NP8**. The first row of ratios shows the ratio of the desired phases NiGa, Ni_2Ga_3, and Ni_3Ga.

(a) The ratios have been calculated from quantified EDX spectra.

	NP5			**NP6**			**NP7**			**NP8**		
	Ni	:	Ga	Ni	:	Ga	Ni	:	Ga	Ni	:	Ga
desired ratio	**1**		**1**	**1**		**1.5**	**1**		**0.33**	**1**		**1**
	1		0.54	1		1.41	1		0.17	1		0.20
	1		0.57	1		1.22	1		0.20	1		0.37
	1		0.64	1		1.25	1		0.20	1		1.45
	1		0.51							1		0.62
	1		0.73							1		1.77

(b) The ratios have been calculated from quantified XPS spectra.[a]

	NP5				**NP7**			
	Ni	:	Ga		Ni	:	Ga	
desired ratio	**1**		**1**		**1**		**0.33**	
sample 1	1		0.85		1		0.13	
	1		0.79		1		0.19	
	1		0.90		1		0.22	
sample 2	1		0.91		1		0.26	
	1		0.68		1		0.15	
	1		0.77		--		--	

[a] Ga-Lines: 2s: 1301 eV
2p1/2: 1144 eV
2p3/2: 1117 eV

Ni-Lines: 2s: 1009 eV
2p1/2: 870 eV
2p3/2: 853 eV

Free-standing NiGa and Ni_3Ga nanoalloy particles obtained from $[Ni(COD)_2]$ and GaCp* in the ionic liquid $[BMIm][BF_4]$

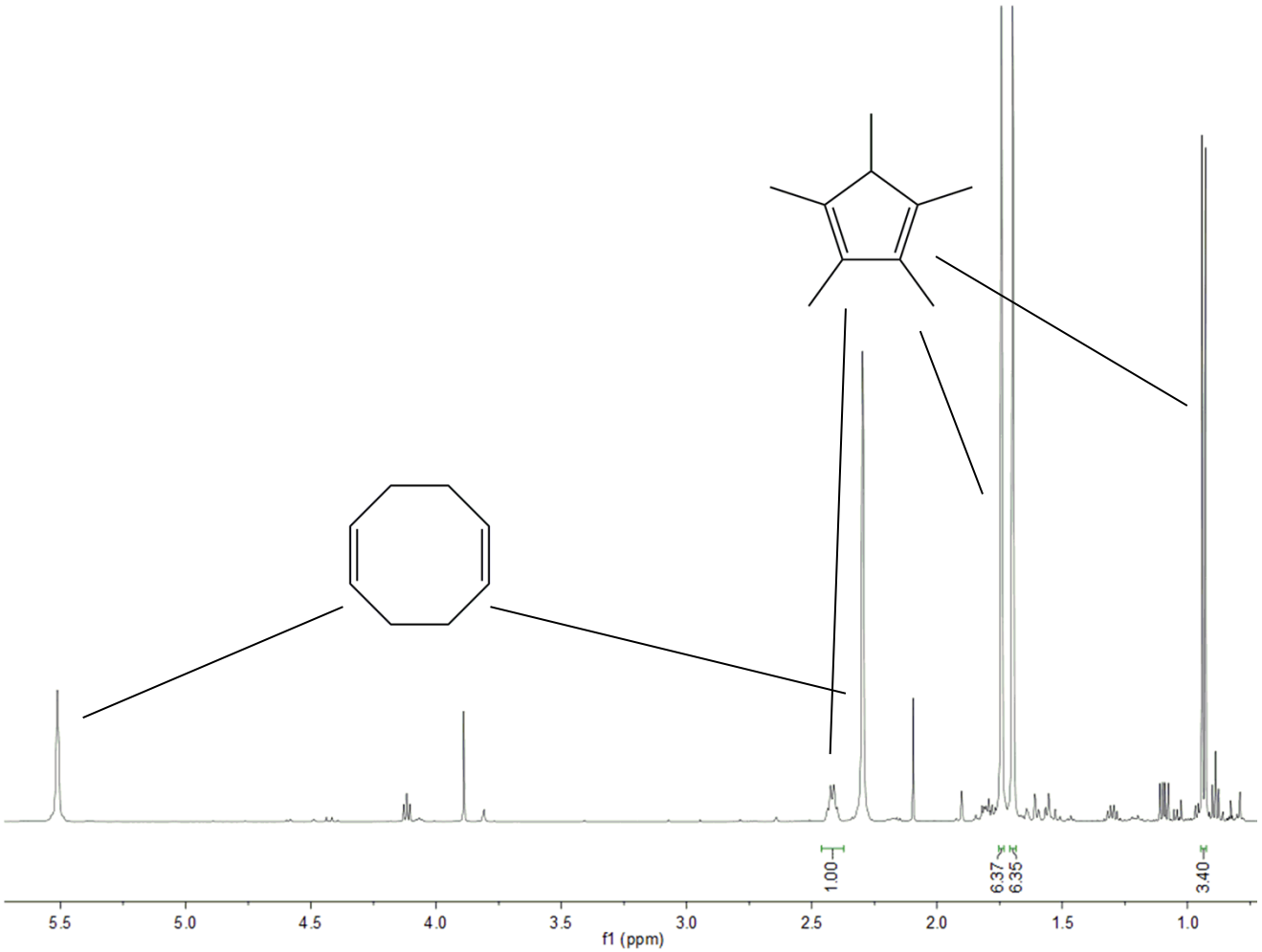


Fig. S17 ^1H NMR spectrum ($CDCl_3$, 600.22 MHz, 298 K) after microwave-assisted co-decomposition of $[Ni(COD)_2]$ and GaCp* in 1:1 molar ratio in $[BMIm][BF_4]$.

Local EDX of NP3-IL

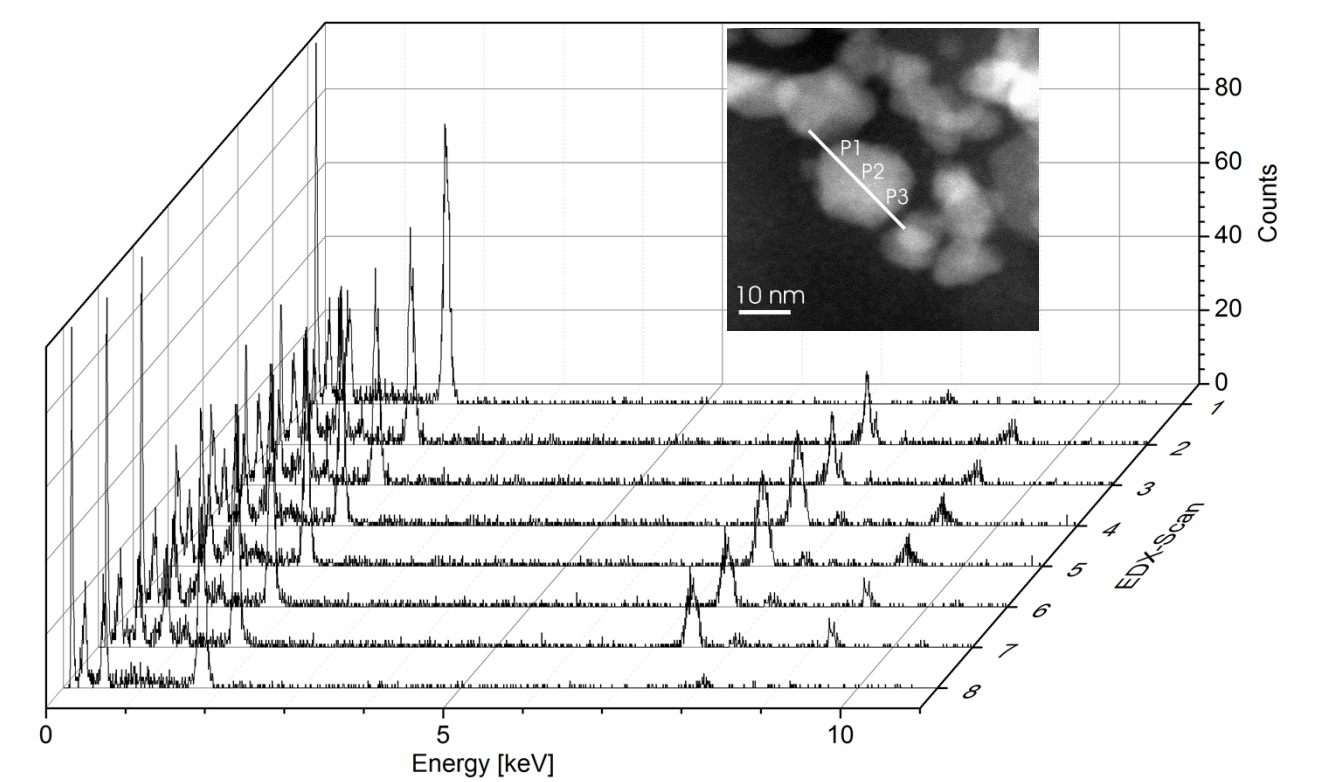
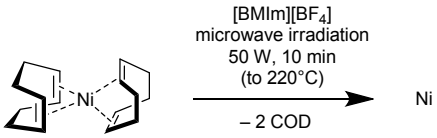


Figure S18 Local energy dispersive X-ray (EDX) spectra of **NP3-IL** recorded over an isolated particle along the white line (TEM picture above) with a 1 nm^2 spatial resolution and an acquisition time of 30 sec.

Table S3 Ratios of Ni to Ga of different selected nanoparticle areas in the samples **NP1-IL and NP3-IL**. The first row of ratios shows the ratio of the desired phases NiGa and Ni_3Ga. The ratios have been calculated from quantified EDX spectra.

	NP1-IL		**NP3-IL**	
	Ni	Ga	Ni	Ga
desired ratio	**1**	**1**	**3**	**1**
	1	1.12	2.91	1
	1	1.06	3.10	1
	1	0.93	2.99	1
	1	1.10	2.92	1

TEM, EDX and PXRD of Ni-NPs from $Ni(COD)_2$ for comparative hydrogenation catalysis



Scheme S1 Microwave induced thermal decomposition of $Ni(COD)_2$ in the absence of H_2 in the ionic liquid [BMIm][BF_4] to nickel nanoparticles (Ni-NPs) as 0.5 wt% Ni/[BMIm][BF_4] for comparative hydrogenation reactions of alkynes.

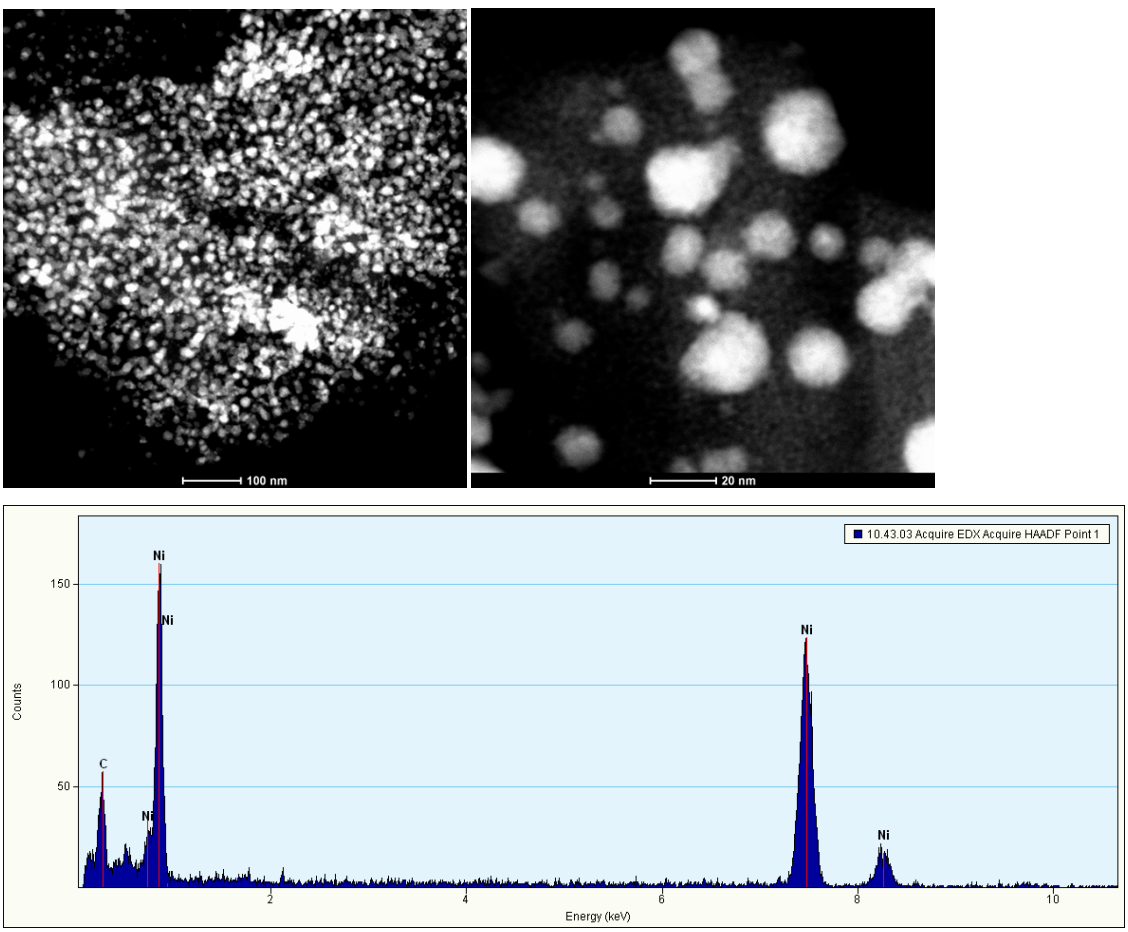


Figure S19 HAADF-STEM images (top) and EDX spectrum (bottom, collected over 70-90 particles) of 0.5 wt% Ni/[BMIm][BF_4] (cf. Scheme S1).

Table S4 Ni-NP size and size distribution. [a]

TEM Ø (σ) [nm][b]	DLS Ø (σ) [nm][b]	PXRD Ø (σ) [nm][b,c]
18 (± 6)	23 (± 4)	15 (± 6)

[a] 0.5 wt. % Ni/[BMIm][BF_4] dispersions obtained by MWI with 50 W for 10 min at 220 °C, cf. Scheme S1. [b] Median diameter (Ø) and standard deviation (σ). See experimental section for TEM and DLS measurement conditions. [c] from Scherrer equation.[3]

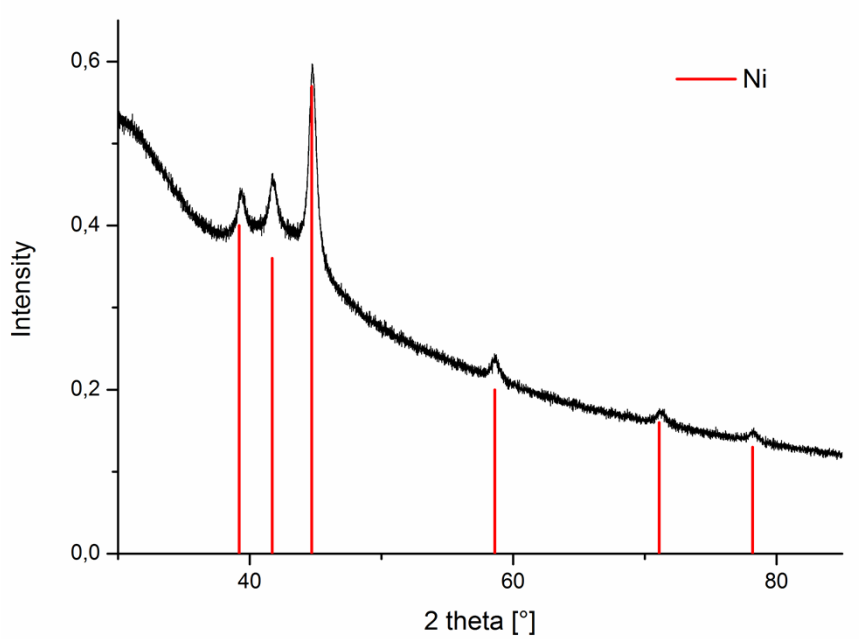


Figure S20 PXRD of 0.5 wt% Ni/[BMIm][BF_4]. Ni reference data in red from COD 9008509.

(Semi-)Hydrogenation of 1-octyne and diphenylacetylene with Ni or NiGa (NP1-IL)

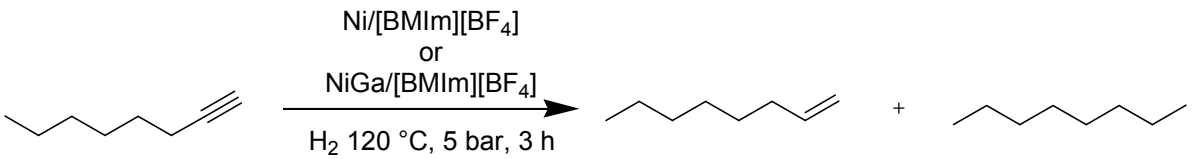


Table S5. (Semi-)Hydrogenation of 1-octyne with Ni or NiGa (NP1-IL).

Sample No.	Catalyst[a]	Temp. (°C)	Conversion (%)	Selectivity (%)		Yield (%)	
				1-Octene	Octane	1-Octene	Octane
i	IL	120	0	-		-	-
ii	Ni/IL	120	96	3	97	3	93
1	NiGa/IL	120	89	93	7	83	6
2	NiGa/IL	120	87	94	6	82	5
3a	NiGa/IL	120	89	92	8	82	7
3b	NiGa/IL	120	90	91	9	85	5
3c	NiGa/IL	120	88	90	10	81	7
3d	NiGa/IL	120	86	90	10	80	6

[a] IL = [BMIm][BF_4]. 0.1g Ni- or NiGa/[BMIm][BF_4] dispersion (0.5 wt% = 0.005 g in total metal, 85 µmol Ni or 39 µmol NiGa) and 2 g (2.5 mL, 18.1 mmol) of degassed, dry 1-octyne, NiGa:substrate ratio = 1:464, Ni:substrate ratio = 1:212. Conversion and selectivity were determined by GC/MS [retention times: 1.51 (1-Octene), 1.67 (octane), 1.87 (1-octyne), Shimadzu GC2014, column: Ultra2, crosslinked 5% PhMe silicone, 25 m x 0.2 mm x 11 µm]. Run 3a-3d was carried out 4 times with the same catalyst by removing the products in high vacuum at 50 °C.

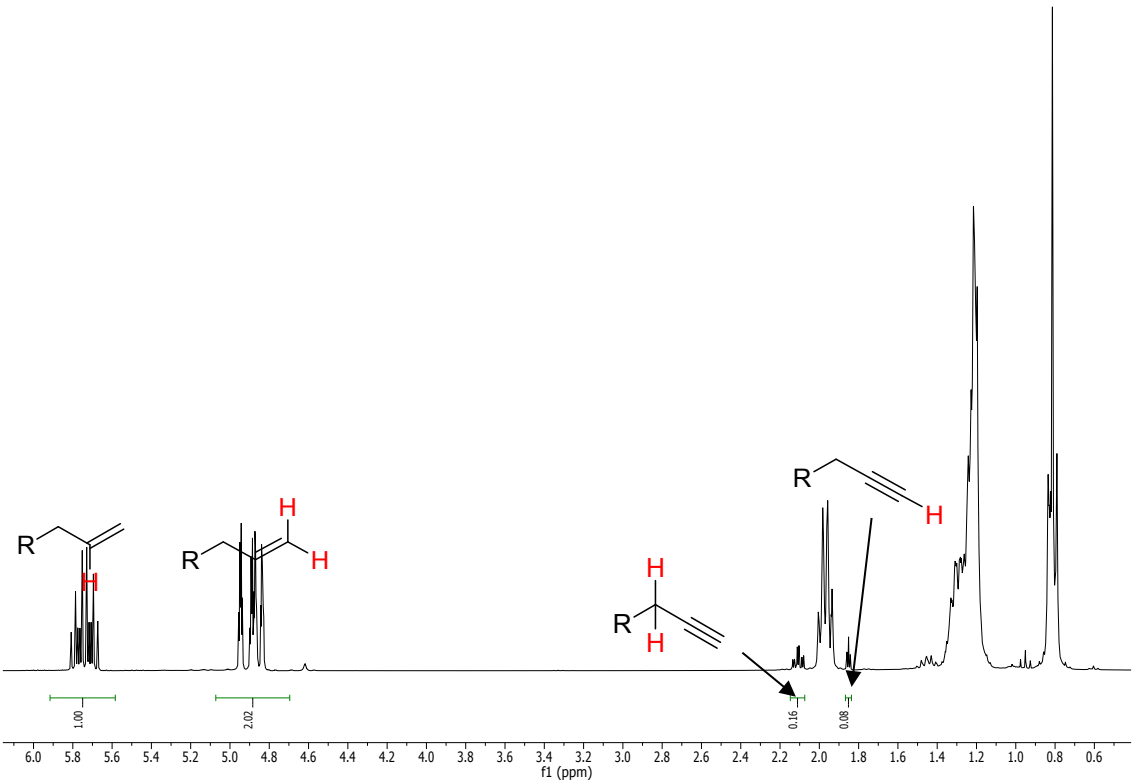


Fig. S21 ^{1}H NMR spectrum ($CDCl_3$) of product mixture of 1-octyne semihydrogenation with 0.1g NiGa/[BMIm][BF_4] dispersion (0.5 wt% = 0.005 g in total metal, 39 µmol NiGa) and 2 g (2.5 mL, 18.1 mmol) of degassed, dry 1-octyne, NiGa:substrate ratio = 1:464, (no. 3); R = C_5H_{11}.

Table S6. (Semi-)Hydrogenation of diphenylacetylene (tolan) with Ni or NiGa (NP1-IL).

Sample No.	Catalyst	Temp. (°C)	Conversion (%)	Selectivity (%)			Yield (%)		
				Diphenyl-ethene	~ethane	side prod.	Diphenyl-ethene	~ethane	side prod.
i	IL	120	0	-			-	-	-
ii	Ni/IL	120	89	8	78	15	7	69	13
1	NiGa/IL	120	90	84	11	4	76	10	4
2	NiGa/IL	120	82	87	10	4	71	8	3

[a] IL = [BMIm][BF_4]. 0.1g Ni- or NiGa/[BMIm][BF_4] dispersion (0.5 wt% = 0.005 g in total metal, 85 µmol Ni or 39 µmol NiGa) and 2 g (11.2 mmol) of tolan, NiGa:substrate ratio = 1:287, Ni:substrate ratio = 1:131. Conversion and selectivity were determined by GC/MS [Shimadzu GC2014, column: Ultra2, crosslinked 5% PhMe silicone, 25 m x 0.2 mm x 11 µm]

References:

1 M. F. Singleton, P. Nash, *Bulletin of Alloy Phase Diagrams.* **1988**, *9*(5), 592-597.
2 H. Okamoto, *J. Phase Equilib. Diffus.*, **2010**, *31*, 575-576.
3 J. I. Langford and A. J. C. Wilson. *J. Appl. Cryst.*, **1978**, *11*, 102-113.