



## Supporting Information

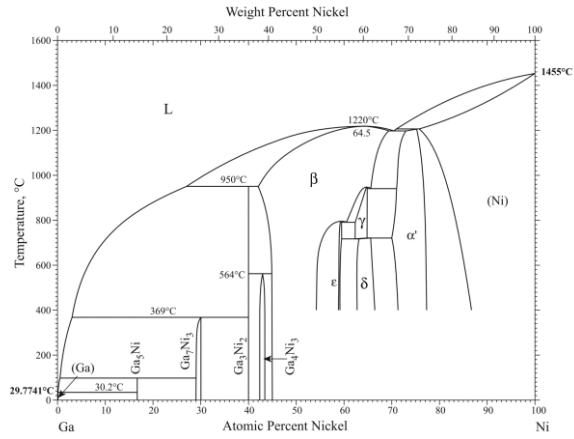
for

### **Synthesis of nickel/gallium nanoalloys using a dual-source approach in 1-alkyl-3-methylimidazole ionic liquids**

Ilka Simon, Julius Hornung, Juri Barthel, Jörg Thomas, Maik Finze, Roland A. Fischer and Christoph Janiak

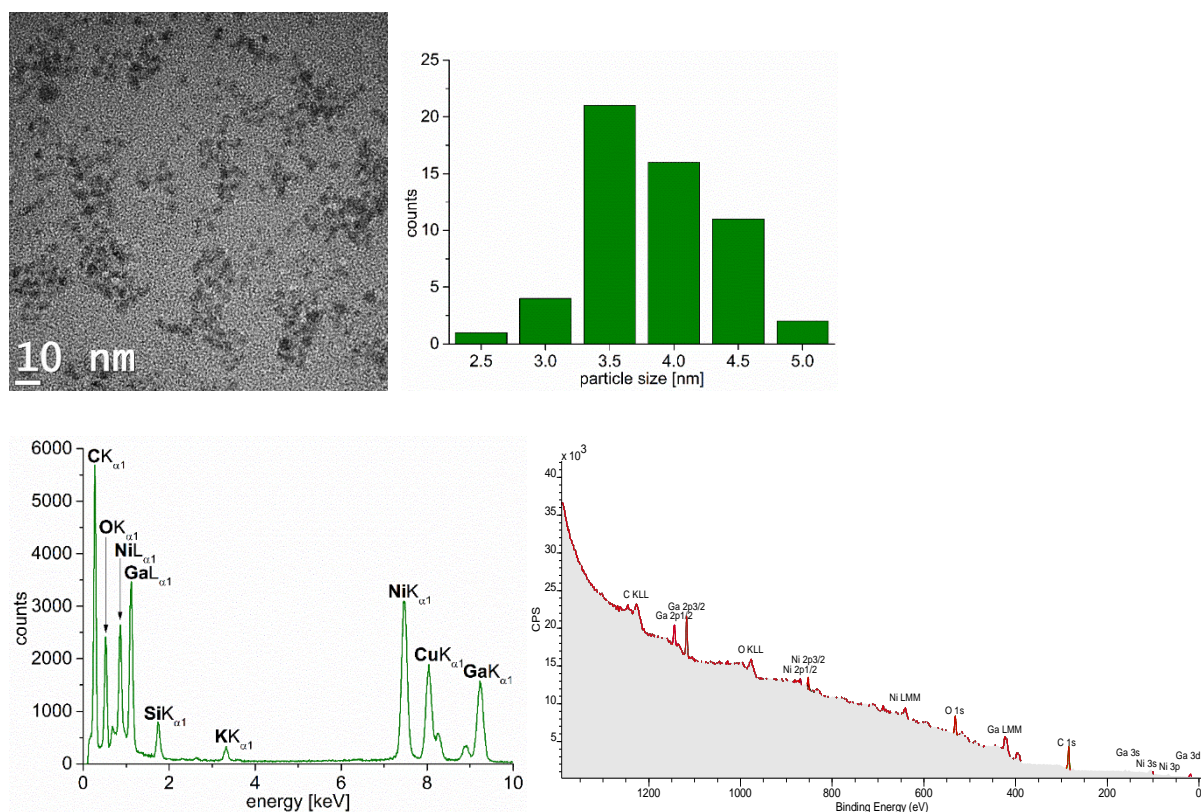
*Beilstein J. Nanotechnol.* **2019**, *10*, 1754–1767. doi:10.3762/bjnano.10.171

## Additional experimental details

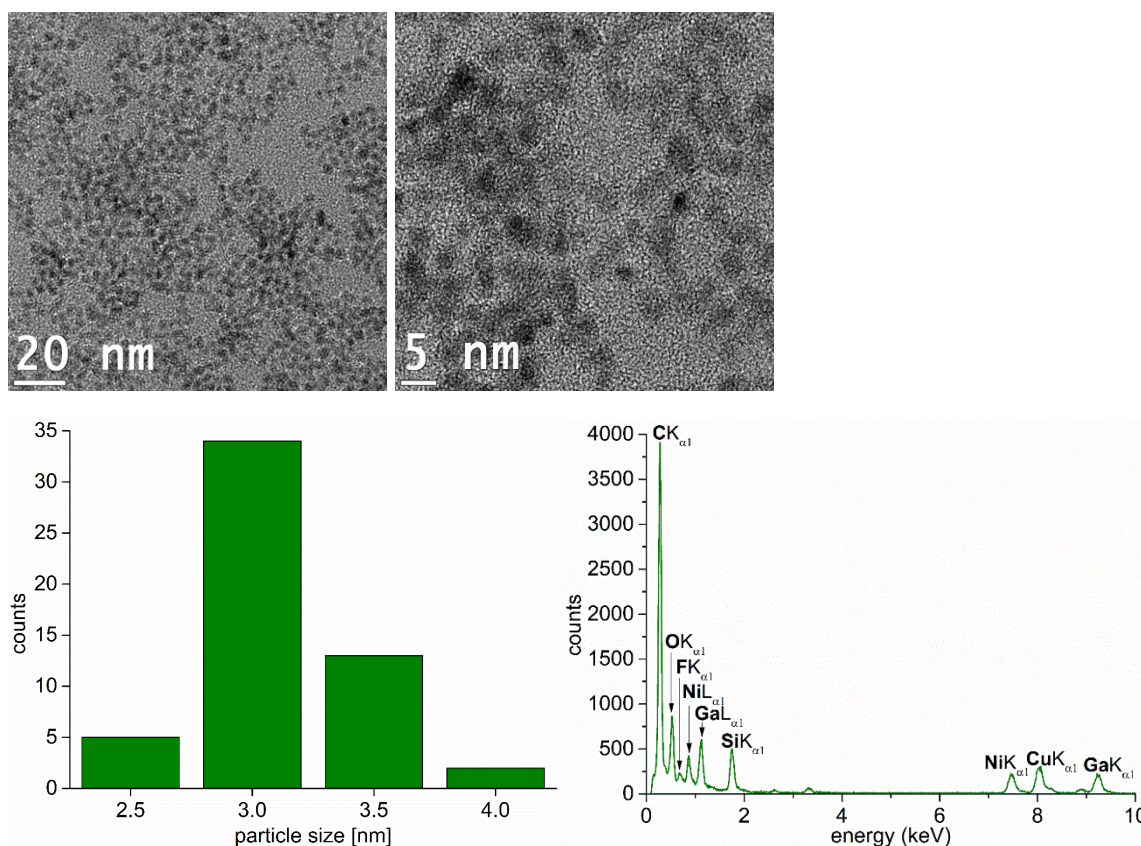


Phase	Composition, at.% Ni	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Ga)	0	<i>oC8</i>	<i>Cmca</i>	<i>A11</i>	Ga
Ga <sub>5</sub> Ni	16.7	...	...	...	...
Ga <sub>7</sub> Ni <sub>3</sub>	29-30	<i>cI40</i>	<i>Im3m</i>	<i>D8<sub>f</sub></i>	Ge <sub>7</sub> Ir <sub>3</sub>
Ga <sub>3</sub> Ni <sub>2</sub>	40	<i>hP5</i>	<i>P3m1</i>	<i>D5<sub>13</sub></i>	Al <sub>3</sub> Ni <sub>2</sub>
Ga <sub>4</sub> Ni <sub>3</sub>	42.4-43.4	<i>cI112</i>	<i>Ia3d</i>	...	...
β	42-69.4	<i>cP2</i>	<i>Pm3m</i>	<i>B2</i>	CsCl
ε	59-59.5	...	...	...	...
γ	62.5-65	<i>hP4</i>	<i>P6<sub>3</sub>/mmc</i>	<i>B8<sub>1</sub></i>	NiAs
δ	63-66.5	<i>oC16</i>	<i>Cmmm</i>	...	Ga <sub>3</sub> Pt <sub>5</sub>
α'	70-77	<i>cP4</i>	<i>Pm3m</i>	<i>L1<sub>2</sub></i>	AuCu <sub>3</sub>
(Ni)	75.7-100	<i>cF4</i>	<i>Fm3m</i>	<i>A1</i>	Cu

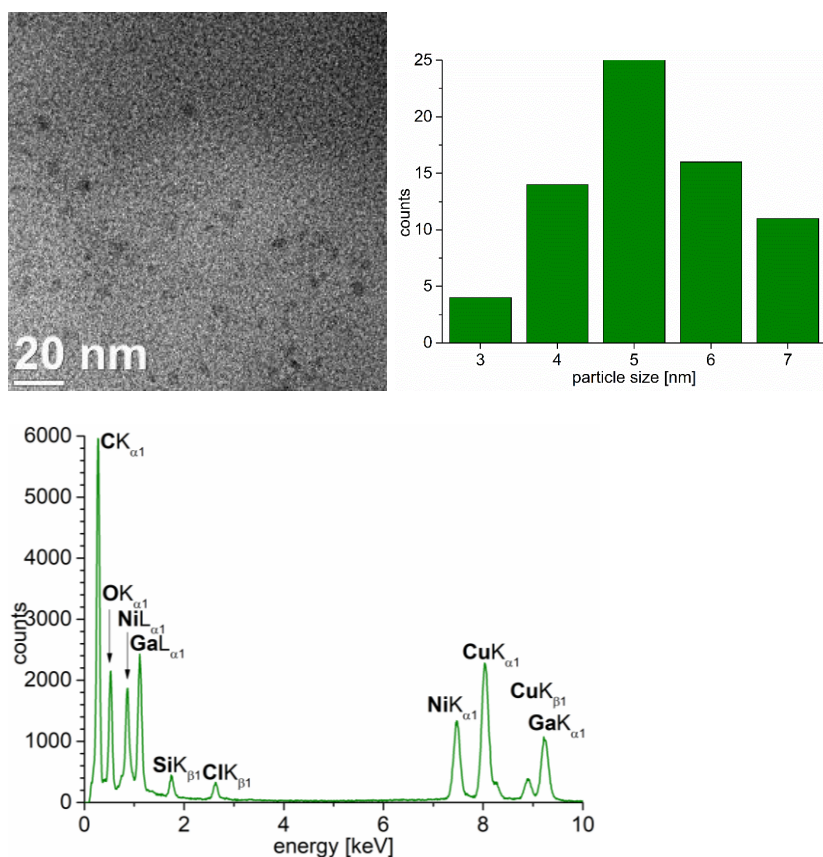
**Figure S1:** Phase diagram and crystal structure data for Ni/Ga taken from literature [1].



**Figure S2:** HR-TEM-Images and particle size distribution of the Ni/Ga-nanoparticles from 1 wt % dispersion of Ni(COD)<sub>2</sub> and GaCp\* in [BMIm][BF<sub>4</sub>] (top) with 24 hours dispersion time, 10 minutes microwave decomposition time. Particle size  $2.5 \pm 0.5$  nm (65 particles counted). EDX- and XP-spectra (bottom). EDX-Quantification from three different spots on the TEM-Grid showed equimolar ratio of nickel to gallium of 41:59 atom % ( $\pm 1$  atom %). No SAED-measurement was possible.



**Figure S3:** HR-TEM-Images of the Ni/Ga-nanoparticles from 0.5 wt % dispersion of  $Ni(COD)_2$  and  $GaCp^*$  in  $[BMIm][BF_4]$  (top) with 24 hours dispersion time, 20 minutes microwave decomposition. Particle size distribution  $2.5 \pm 0.5$  nm (56 particles counted) and EDX-spectra (bottom). EDX-Quantification from three different spots on the TEM-Grid showed equimolar ratio of nickel to gallium of 57:43 atom % ( $\pm 2$  atom %). No SAED-measurement was possible.



**Figure S4:** HR-TEM-Images and particle size distribution of the Ni/Ga-nanoparticles from 0.5 wt-% dispersion of  $\text{Ni}(\text{COD})_2$  and  $\text{GaCp}^*$  in propylene carbonate (PC). 24 hours dispersion time before decomposition, 20 minutes microwave decomposition. Particle size  $5 \pm 1$  nm (70 particles counted). EDX-Quantification from three different spots on the TEM-Grid showed equimolar ratio of nickel to gallium of 45:55 atom % ( $\pm 1$  atom %). No SAED-measurement possible.

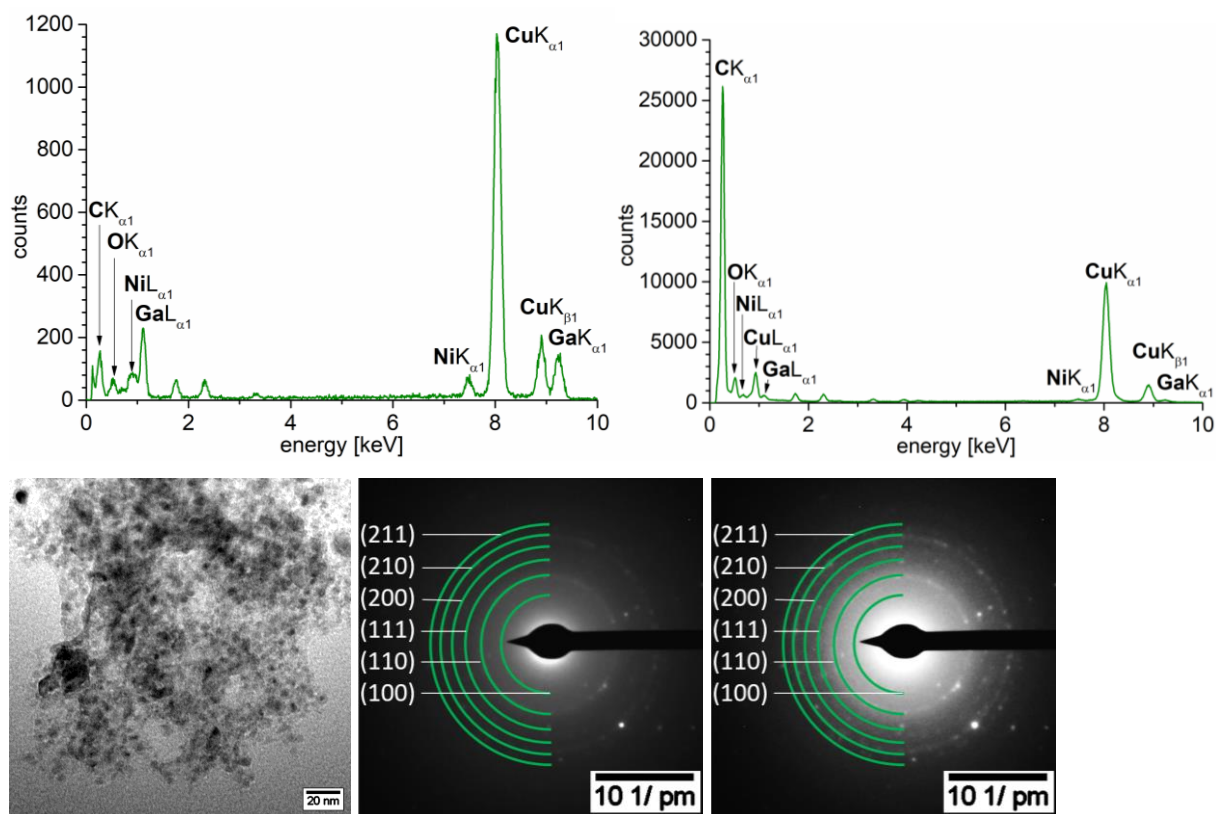
**Table S1:** Comparison of d-spacing values (hkl-index) of experimental results (exp.) vs NiGa, Ga and Ga-rich phases. For literature d-spacing values the nine most intense reflections were chosen.

exp.	NiGa [ <i>Pm</i> $\bar{3}$ <i>m</i> ]	Ga [ <i>Cmce</i> ]	Ni <sub>3</sub> Ga <sub>4</sub> [ <i>Ia</i> $\bar{3}$ <i>d</i> ]	Ni <sub>2</sub> Ga <sub>3</sub> [ <i>P</i> $\bar{3}$ <i>m</i> ]	Ni <sub>3</sub> Ga <sub>7</sub> [ <i>Im</i> $\bar{3}$ <i>m</i> ]	NiGa <sub>5</sub> [ <i>I4/mcm</i> ]
0.398		0.382 (020)	0.466 (211)	0.489 (001) 0.351 (100)	–	–
0.283	0.288 (100)	0.294 (111)	0.305 (321) 0.285 (400)	0.285 (101)	0.267 (310) 0.244 (222)	0.271 (211)
0.231		0.225 (200)	–	–	0.226 (321)	0.223 (220) 0.213 (114/213)
0.201	0.204 (110)	0.199 (131)	0.208 (521) 0.202 (440)	0.203 (110) 0.201 (102/012)	0.199 (330/411)	0.200 (310) 0.193 (204)
0.181		0.178 (221)	–	–	0.189 (420)	–
0.164	0.167 (111)		0.165 (444)	–	0.172 (422)	–
0.141	0.144 (200)	0.140 (023)	0.143 (800)	0.143 (202)	0.149 (440) 0.141 (600)	–
0.134	0.129 (210)		–	–	–	0.132 (404)
0.127		0.124 (331) 0.122 (152)	0.128 (840)	–	–	0.127 (334) 0.125 (217)
0.121	0.118 (211)	0.119 (223)	0.117 (844)	0.117 (300) 0.117 (122/21 $\bar{2}$ ) 0.115 (104)	0.115 (633)	–

**Table S2:** EDX-quantification results from NiGa- and Ga(Ni)-nanoparticles in [BMIm][NTf<sub>2</sub>], 1 hour and 12 hours dispersion time.

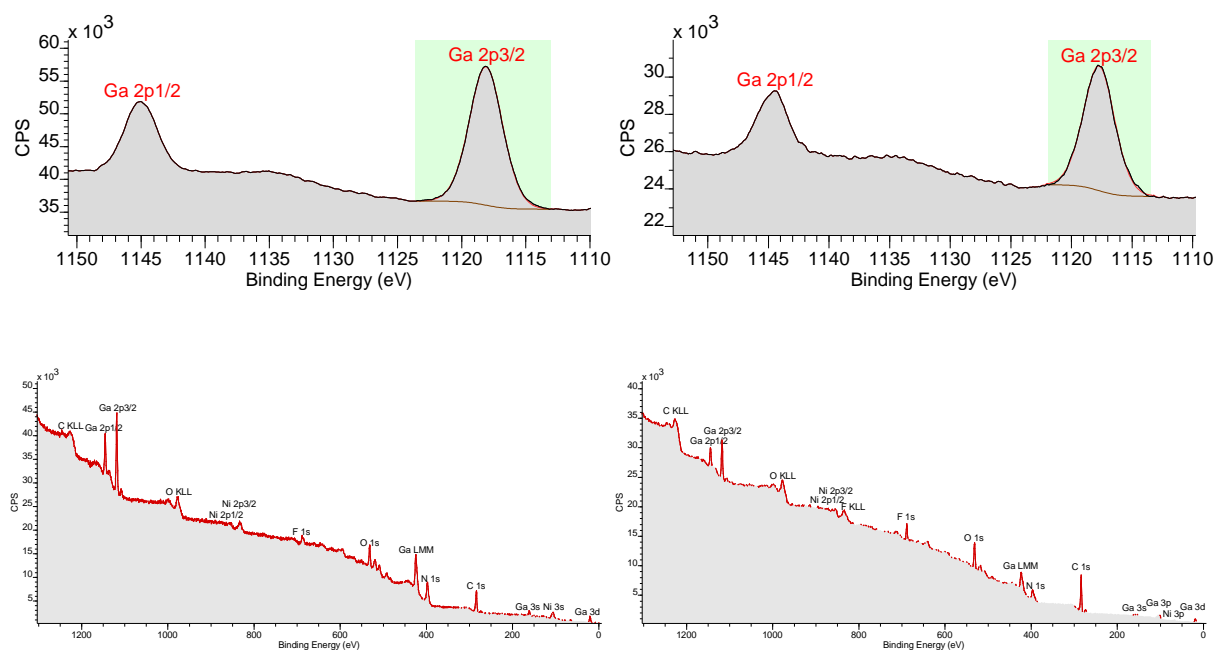
mostly large Ga(Ni)- next to some small NiGa-nanoparticles in [BMIm][NTf <sub>2</sub> ], 1 hour dispersion time					
spot number	#1	#2	#3	Ø	σ
Ni (K) [%]	28	24	30	28	2
Ga (K) [%]	72	76	70	72	2
NiGa- and Ga(Ni)-nanoparticles in [BMIm][NTf <sub>2</sub> ], 12 hour dispersion time					
spot number	#1	#2	#3	Ø	σ
Ni (K) [%]	36	38	40	38	1
Ga (K) [%]	64	62	60	62	1



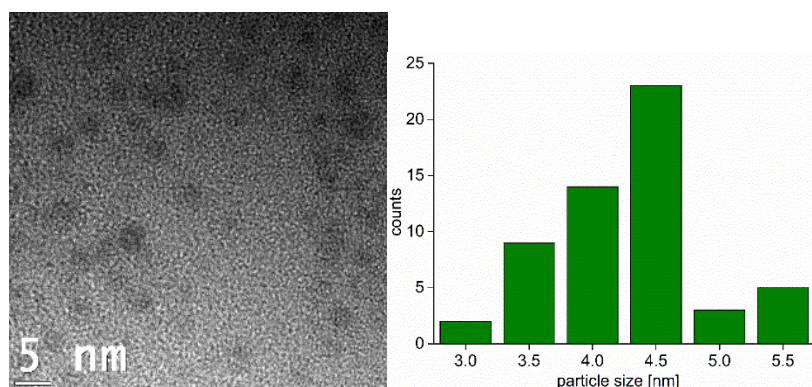


**Figure S5:** Top: EDX-spectra of mostly large Ga(Ni)-nanoparticles (left) and only small NiGa-nanoparticles (right) from a 0.5 wt % dispersion of Ni(COD)<sub>2</sub> and GaCp\* in [BMIm][NTf<sub>2</sub>] after 1 hour dispersion time prior to 30 min decomposition. Bottom: HR-TEM-image of NiGa-nanoparticles. SAED with indexed reflections for NiGa (green diffraction rings for space group  $Pm\bar{3}m$ ) with two different contrasts.

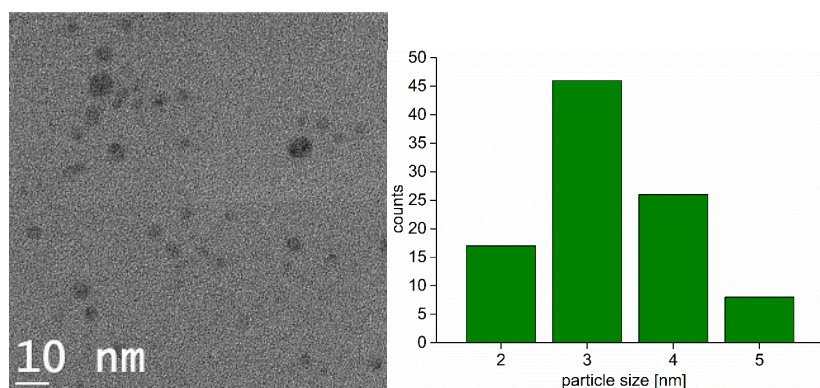




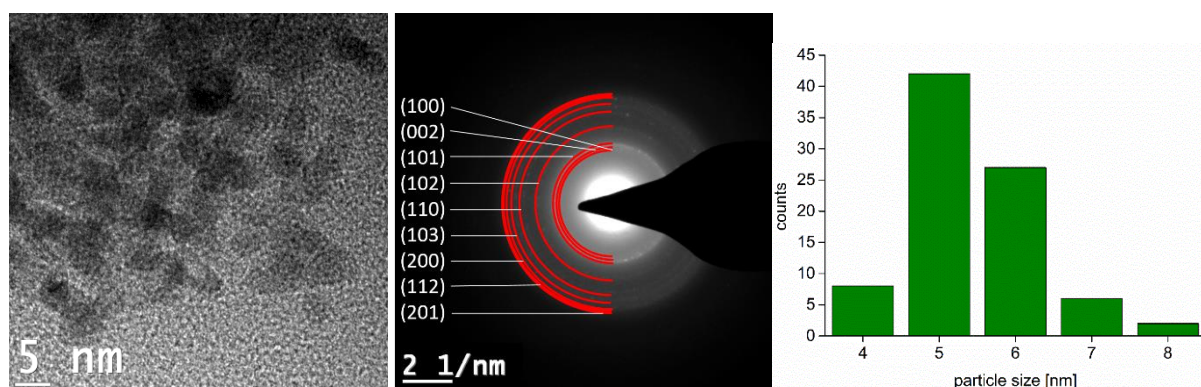
**Figure S6:** Top: HR-XPS-spectral region of the Ga 2p<sub>1/2</sub> and 2p<sub>3/2</sub>-orbital of NiGa/ Ga(Ni)-nanoparticles samples obtained by microwave-induced decomposition after 1 hour dispersion time (left) and 12 hours dispersion time (right). Bottom: full XPS-spectra of NiGa/ Ga(Ni)-nanoparticles samples obtained by microwave-induced decomposition after 1 hour dispersion time (left) and 12 hours dispersion time (right).



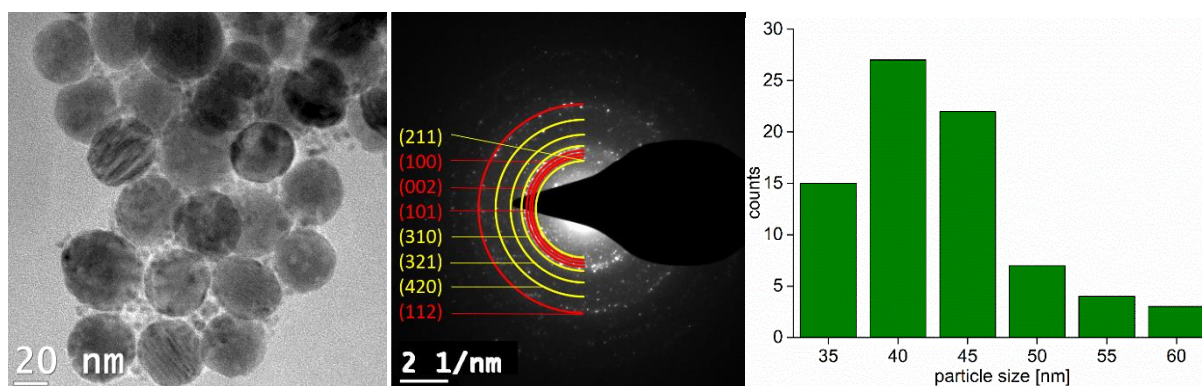
**Figure S7:** HR-TEM-Images and particle size distribution of the Ni-nanoparticles from 1 wt % dispersion of Ni(COD)<sub>2</sub> and GaCp\* in [EMIm][B(CN)<sub>4</sub>]. 30 minutes dispersion time, 30 minutes microwave decomposition. Particle size: 4 ± 1 nm (56 particles counted). EDX-Quantification from three different spots on the TEM-Grid showed only nickel. No SAED-measurement possible.



**Figure S8:** HR-TEM-Images and particle size distribution of the Ni/Ga-nanoparticles from 1 wt % dispersion of  $\text{Ni(COD)}_2$  and  $\text{GaCp}^*$  in  $[\text{EMIm}][\text{B(CN)}_4]$ . 24 hours dispersion time, 30 minutes microwave decomposition. Particle size:  $4 \pm 1$  nm (97 particles counted). EDX-Quantification from different spots on the TEM-Grid showed No SAED-measurement possible.

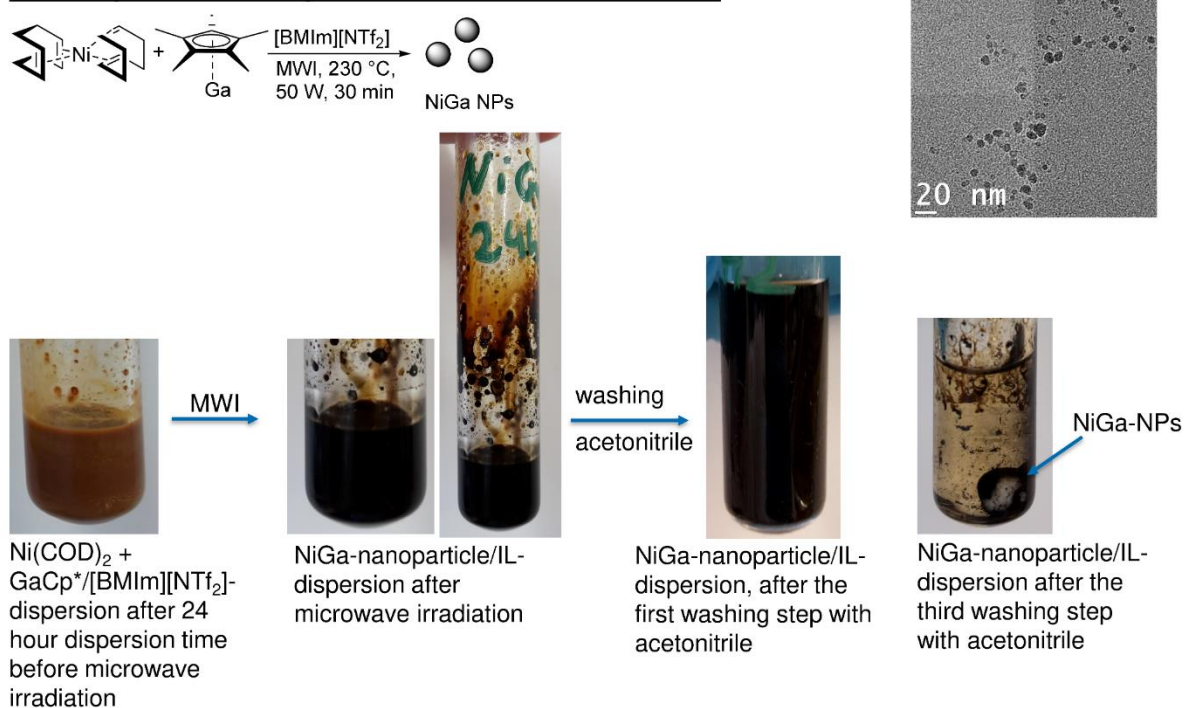


**Figure S9:** TEM-image and particle size distribution of 1.0 wt % Ni-nanoparticles in  $[\text{EMIm}][\text{FB(CN)}_3]$  from  $\text{Ni(COD)}_2$  and  $\text{GaCp}^*$ . 1 hour dispersion time, 30 minutes microwave decomposition. SAED with indexed reflections for Ni (space group:  $P6_3/mmc$ ), particle size:  $5 \pm 1$  nm (85 particles counted). EDX-Quantification from this spot showed ratio of nickel to gallium of 87:13 atom % ( $\pm 1$  atom %).



**Figure S10:** TEM-image and particles size distribution of 1.0 wt % Ni- and Ga(Ni)-nanoparticles in [EMIm][FB(CN)<sub>3</sub>] from Ni(COD)<sub>2</sub> and GaCp\*. 1 hour dispersion time, 30 minutes microwave decomposition. SAED with indexed reflections for Ni (red diffraction rings for space group:  $P6_3/mmc$ ) and Ga (yellow diffraction rings for space group:  $\bar{1}43d$ ), particle size: Ni:  $5 \pm 1$  nm, Ga(Ni):  $40 \pm 5$  nm. EDX-Quantification from this spot showed ratio of nickel to gallium of 49:51 atom % ( $\pm 1$  atom %).

**24 h dispersion of the precursors in the IL before MWI**



**Figure S11:** preparation of NiGa-nanoparticles from 24 hour dispersion time and 30 minutes decomposition time.

**Table S3:** Semihydrogenation of 4-octyne to 4-octene using IL-free, precipitated NiGa-nanoparticles in comparison to NiGa@[BMIm][NTf<sub>2</sub>].<sup>a</sup>

	NiGa-nanoparticles				NiGa@[BMIm][NTf <sub>2</sub> ]			
	conversion	selectivity	TON	TOF	conversion	selectivity	TON	TOF
	4-octene				4-octene			
	[%]	[%]	–	[h <sup>-1</sup> ]	[%]	[%]	–	[h <sup>-1</sup> ]
run 1	93–96	82–89	157	170	15-19	100	384	128
run 2	92–93	95–100	175	211	10	100	322	107
run 3	82–92	96–100	143	154	20	100	558	186

<sup>a</sup> 0.1 g NiGa@[BMIm][NTf<sub>2</sub>] dispersion (1 wt % = 0.001 g in total metal, 7.8 μmol NiGa) and 2 g (2.7 mL, 18.2 mmol) of degassed dry 4-octyne (molar NiGa:substrate ratio = 1:2331) were stirred under 5 bar H<sub>2</sub> at 120 °C for 3 h. Runs 1–3 were carried out with the same catalyst by removing the products in high vacuum. In a typical catalytic test reaction 10 mg precipitated, IL-free NiGa-nanoparticles (77 μmol) and 1 g (1.35 mL, 9 mmol) of degassed dry 4-octyne (molar NiGa:substrate ratio = 1:115) were stirred under 5 bar H<sub>2</sub> at 120 °C. Runs 1–3 were carried out with the same catalyst by removing the products in high vacuum. TON per run (TON = mol<sub>substrate</sub>/mol<sub>catalyst</sub>). TOF [h<sup>-1</sup>] per run (TOF = mol<sub>substrate</sub>/(mol<sub>catalyst</sub>\*time)).

**Table S4:** Mass of Ni(COD)<sub>2</sub>, GaCp\* IL and PC, wt % total metal dispersion, dispersion and decomposition times in IL or PC.

IL/PC	IL/PC g (mL)	Ni(COD) <sub>2</sub> mg (mmol)	GaCp* mg (mmol)	wt % total metal dispersion	dispersion time [h]	decomp. time [min]
[BMIm][BF <sub>4</sub> ]	1.9341 (1.51)	43.1 (0.157)	31.8 (0.154)	0.995	24	10
[BMIm][BF <sub>4</sub> ]	1.2012 (0.94)	13.1 (0.048)	9.8 (0.048)	0.499	24	20
[BMIm][NTf <sub>2</sub> ]	1.2064 (0.84)	13.1 (0.048)	10 (0.049)	0.502	24	10
[BMIm][NTf <sub>2</sub> ]	0.9998 (0.70)	12.6 (0.046)	8.2 (0.040)	0.544	24	30
[BMIm][NTf <sub>2</sub> ]	1.0057 (0.70)	11.7 (0.043)	10.3 (0.050)	0.572	1	30
[BMIm][NTf <sub>2</sub> ]	1.0023 (0.70)	22.3 (0.081)	19.4 (0.094)	1.066	12	30
PC	1.2001 (1.00)	13.1 (0.048)	10.0 (0.0049)	0.504	24	20
[EMIm][B(CN) <sub>4</sub> ]	1.0015 (0.96)	22.4 (0.081)	18.4 (0.089)	1.0045	0.5	30
[EMIm][B(CN) <sub>4</sub> ]	0.2533 (0.24)	8.8 (0.032)	6.2 (0.030)	1.493	24	20
[EMIm][BF(CN) <sub>3</sub> ]	1.0045 (0.94)	22.5 (0.082)	17.6 (0.085)	1.025	1	30
[EMIm][BF(CN) <sub>3</sub> ]	0.3156 (0.19)	10.6 (0.039)	7.9 (0.038)	1.478	24	30
[BMIm][NTf <sub>2</sub> ]	1.0586 (0.74)	–	15.6 (0.076)	0.492	24	60

<sup>1</sup> H. Okamoto, *J. Phase Equilib. Diffus.* **2010**, 31, 575–576.