# **Supporting Information**

Matching the organic and inorganic counterparts during nucleation and growth of copper-based nanoparticles – in situ spectroscopic studies

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## 1. EXAFS – normalization parameters

	Pre-edge range		Normalization range		Eo	Range in k	
	pre-1	pre-2	post-1	post-2	0	k-1	k-2
Cu	8850.73	8939.82	9147.69	9792.89	8978.43	2.3	12.633
$Cu(acac)_2$	8857.73	8953.76	9077.3	9788.79	8983.76	2.3	12.633
CuO	8851.48	8941.92	9072.85	9794.99	8983.23	2.3	12.633
Cu <sub>2</sub> O	8856.93	8930.67	9090.65	9795.54	8979.88	2.3	12.633
Cu(OH) <sub>2</sub>	8654.54	8920.10	9040.08	10091.05	8987.50	2.3	15.019

Table S1 Normalization parameters used in EXAFS

### 2. MCR-ALS method

### (a) XANES data

Table S2 SVD results for the analysis of XANES spectra for ten first components.

Number of components	Eigen Values	
1	114.32	
2	7.56	
3	2.01	
4	0.51	
5	0.46	
6	0.17	
7	0.14	
8	0.14	
9	0.13	
10	0.12	

## Table S3 The MCR-ALS results of the XANES spectra analysis.

Standard deviation of residuals	0.010675
Fitting error (lack of fit), %	1.1145
Percent of variance explained at the optimum	99.9876

### (b) FTIR data

All absorption spectra were corrected for the baseline offset due to particle deposition on the probe. First we shifted the spectra on y-axis that the data point at the  $1800 \text{ cm}^{-1}$  was at zero and then by 0.03 and 0.1 for synthesis at 140 and 170 °C, respectively.

Due to the particle deposition on the probe, the measurements were paused. Therefore the in situ data were divided into two sets. For the reaction at 140 °C first set contains spectra recorded before the particle deposition (from 0 to 514 minutes) and the second set contains spectra recorded after the deposition until the cleaning of the probe (from 516 to 2758 minutes). For the reaction at 170 °C the first set and the second set contains spectra before the cleaning procedure – from 0 to 60 minutes and after the cleaning procedure – from 72 to 326 minutes, respectively.

To find the time at which particles start to deposit on the ATR crystal of the FTIR probe, we plot the absorption changes at 850 cm<sup>-1</sup> (Figure S1). At this wavelength we do not observe any IR absorption bands characteristic for species in the solution. After 514 minutes the intensity at 850 cm<sup>-1</sup> starts to decrease, which indicates the beginning of particle deposition.



**Figure S1** Intensity changes at 850 cm<sup>-1</sup> as a function of reaction time during synthesis at 140 °C.

We use SIMPLISMA algorithm, which is a variance-based method, to find the initial FTIR spectra of the components, whose concentration significantly differ from scan to scan, compared to other components. Thus, the FTIR spectrum of the single component, recovered by the ALS algorithm and shown in Figure S2, do not necessarily directly correspond to the spectrum of the single chemical compounds. The corresponding concentration profiles of MCR-ALS recovered components are shown in Figure S3a-b.



**Figure S2** In situ FTIR spectra recorded during the synthesis of copper based nanoparticles from  $Cu(acac)_2$  in benzyl alcohol (a) at 140 °C and (b) at 170 °C. The spectra of components recovered with MCR-ALS and of the corresponding references (c) at 140 °C and (d) at 170 °C.

We emphasize the characteristic vibrations of species being formed during the reaction by comparing consecutively recovered spectra in Figure S2c-d. Note that we use the spectrum of benzyl alcohol as a baseline and thus its characteristic vibrations are neither visible in Figure S2, nor discussed in the following text. The spectra of the first three components for both temperatures are very similar. The spectrum of the first component is the spectrum of the precursor with characteristic v(Cu-O), v(C-C-C)and  $v(CH_3)$  vibrations of metal acetylacetonate in the range from 1580 to 1250 cm<sup>-1</sup>. The spectrum of the second component, in addition to the characteristic bands of the precursor, shows a broad band from 1200 to 1050 cm<sup>-1</sup>, a small shoulder at 1551 cm<sup>-1</sup>, and multiple bands between 1700 and 1750 cm<sup>-1</sup>. The origin of the broad absorption at 1200-1050 cm<sup>-1</sup> is not fully clear, however absorption in this frequency region indicates the v(C-O) vibration of benzyl alcohol, which is normally observed at 1020 cm<sup>-1,1</sup> We propose that this downshift manifests the complexation of benzyl alcohol with Cu(acac)<sub>2</sub>, which is in line with the aforementioned changes in XANES and UV-Vis spectra. The band at 1551 cm<sup>-1</sup> originates from double overtone of the C-H deformation vibration at the carbon ring of the acetylacetonate species. Generally, shifting of its position and changes of intensity manifest hydrogen bonding of protic solvents.<sup>2</sup> The multiple bands between 1700 and 1750 cm<sup>-1</sup> are characteristic for v(C=O) vibrations of benzaldehyde and benzyl acetate. In the spectra of the third component, the multiple bands between 1700 and 1750 cm<sup>-1</sup>, already observed in the spectra of the second components, are even more pronounced. Additionally, we note a slight shifting of the v(C-O) and v(C-C-C) stretching vibrations of Cu(acac)<sub>2</sub>. It indicates that the presence of benzaldehyde and benzyl acetate in the reaction solution alter the interaction of the carbonyl carbon in the acetylacetonate ligand with benzyl alcohol The spectra of components 4 and 5, recovered from the measurements at 140 and 170 °C, strongly differ. In the spectrum of component 4 at 170 °C, we no longer observe the characteristic vibration of Cu(acac)<sub>2</sub>, which means that all the precursor is used up. Instead we observe only benzyl acetate or benzaldehyde. Additionally, at 140 °C we observe new bands at 1108 cm<sup>-1</sup>, which we assign to benzyl alcoholate adsorbed at the surface of Cu<sub>2</sub>O.<sup>3-5</sup> At 170 °C, in addition to characteristic vibration of benzyl acetate and benzaldehyde, we observe new bands at 1096 and 1070 cm<sup>-1</sup>, which we assign to v(C-O) stretching vibrations of dibenzyl ether. For further discussion please see below, paragraph 3 "Organic species at the surface of nanoparticles".

The results of SVD and ALS optimization of the FTIR data analysis are shown in Table S4 and Table S5, respectively. Each set was fitted with three components. The concentration profiles of recovered spectra are presented in Figure S3a-b. The last recovered spectrum of the first set and the first recovered spectrum of the second set for both temperatures, shown in Figure S3c-d are identical. Therefore are considered as only one component – component 4.

	Eigen Values				
Number of	14	•0 °C	170 °C		
components	First set of	Second set of	First set of	Second set of	
	spectra	spectra	spectra	spectra	
1	16.09	27.42	31.95	52.39	
2	1.11	4.37	0.79	1.53	
3	0.21	2.11	0.08	0.38	
4	0.05	0.84	0.04	0.18	
5	0.04	0.20	0.03	0.13	
6	0.03	0.10	0.03	0.09	
7	0.02	0.06	0.03	0.08	
8	0.02	0.04	0.03	0.07	
9	0.01	0.03	0.03	0.05	
10	0.01	0.03	0.03	0.05	

Table S4 SVD results for the analysis of FTIR spectra for ten first components.

 Table S5 MCR-ALS results of FTIR data.

	140 °C		170 °C	
	First set of spectra	Second set of spectra	First set of spectra	Second set of spectra
Standard deviation of residuals	0.000444	0.0011811	0.0018638	0.0012588
Fitting error (lack of fit), %	1.0251	3.2908	1.3822	1.1505
Percentage of variance explained at the optimum	99.9895	99.8917	99.989	99.9868





Figure **S3** Concentration components recovered with MCR-ALS for the synthesis (a) at 140 °C and (b) at 170 °C. Spectra of last and first component recovered with MCR-ALS method from the first set and second set of data recorded at (c) 140 °C and (d) 170 °C.

### 3. Organic species adsorbed at the surface of Cu<sub>2</sub>O

At 140 °C, in addition to the characteristic vibration of benzyl acetate and benzaldehyde, we observe new band at 1618 cm<sup>-1</sup>, which we assign to benzyl alcohol strongly bonding to the surface of Cu<sub>2</sub>O.<sup>4, 6, 7</sup> In order to analyze the spectrum of organics announced by large absorption band at 1618 cm<sup>-1</sup> we subtract the spectrum recorded shortly before the probe was cleaned from the spectrum after (Figure S4a). In the differential spectrum (Figure S4b) in addition to 1618 cm<sup>-1</sup> band we observe bands at 1320 and 1364 cm<sup>-1</sup>, which we assign to the phenyl ring vibrations of benzyl alcohol. They are downshifted from their original position due the interaction of the phenyl ring with OH groups on newly synthesized Cu<sub>2</sub>O surface.



**Figure S4** In situ FTIR spectra recoded during the reaction at 140 °C: (a) Spectra recorded shortly before (black curve) and after (red curve) probe cleaning and (b) their difference spectra.



**Figure S5** In situ UV-Vis spectra recorded during the synthesis of copper based nanoparticles from Cu(acac)<sub>2</sub> in benzyl alcohol (a) at 140 °C, from 207 to 327 minutes; (b) and (c) at 170 °C, from 0 to 27 minutes and from 41 to 62 minutes, respectively

#### 4. UV-VIS analysis

In UV-Vis we can distinguish between different species based on the characteristic absorption. For bulk Cu<sub>2</sub>O and CuO the characteristic UV-vis absorption due to the band gap are observed at 2.17 eV (517 nm) and 1.2 eV (1033 nm), respectively. These values increase with the decrease in nanoparticle size, even by about 0.6 eV.<sup>8-13</sup> For metallic copper, the characteristic UV-Vis absorption at around 600 nm is exclusively due to the surface plasmon resonance in reduced dimensions.<sup>3, 14</sup>

After addition of the precursor to the preheated benzyl alcohol we observe an absorption with a maximum around 310 nm, which originates from the Cu(acac)<sub>2</sub> complexes in benzyl alcohol as shown in Figure S5a-b.53 This is in line with aforementioned XANES studies. At 140 °C after 209 minutes of reaction we observe an absorption band with a maximum at 440 nm, increasing in intensity and shifting to higher wavelengths with reaction time. The dotted lines in the Figure S5 helps as a guideline to the eye. Simultaneously, the intensity of the peak at 310 nm decreases. This reflects reduction of Cu(acac)<sub>2</sub> and nucleation and growth of cuprous oxide nanoparticles. After around 330 minutes no further changes are observed. At 170 °C, the reduction is much faster and already after 17 minutes we observe the formation of cuprous oxide nanoparticles and their consecutive growth. Additionally, after 52 minutes we observe a new broad peak at 632 nm, which indicates the formation of metallic copper nanoparticles. Thus, we conclude that qualitatively the UV-Vis measurements are in line with XAS studies. For UV-Vis experiments we cannot derive the concentration profiles due to experimental constraints related to the deposition of the nanoparticles on the probe. For further details see the experimental section.



**Figure S6** Gas chromatograms of the final reaction liquid from the synthesis of copper based nanoparticles from copper(II) acetylacetonate in benzyl alcohol (a) at 140  $^{\circ}$ C and (b) at 170  $^{\circ}$ C. Gas chromatograms of reaction liquid from control experiment (c) at 140  $^{\circ}$ C after 50 hours and (d) at 170  $^{\circ}$ C after 5 hours.

We note that in the initial experiments we had identified the benzaldehyde dibenzyl acetal in reaction solution. However, after replacing benzyl alcohol with benzyl alcohol from another batch the benzaldehyde dibenzyl acetal species vanished. Its presence in solution has no influence on the occurrence and quantity of other compounds forming during synthesis, thus we do not discuss its formation in the main text.

#### 6. Calibration Curves

We made the calibration curves by using the absorbance of most prominent peak of corresponding organic species shown in Figure S7. To follow the reaction conditions, each standard was measured in benzyl alcohol preheated to a corresponding temperature and spectrum of benzyl alcohol was used as a baseline. Due to slight shifting of the recorded peak absorbance during the synthesis in comparison with the corresponding references, for each standard measurement we average the absorbance value in the range given in Table S6. The Limit of Detection (LOD) was defined as three times standard deviation of the blank measurement. For the Cu(acac)<sub>2</sub>, due to its instantaneous reaction with preheated benzyl alcohol, we evaluate its concentration assuming that the intercept is 0 and the 0.070 M corresponds to the absorbance value recorded immediately after the precursor was added to the preheated benzyl alcohol. **Table S6** Averaged area of organic references used in calibration curve.

Compound	Averaged ranged	Vibration mode
Benzaldehyde	$1700 - 1708 \text{ cm}^{-1}$	υ(C=O)
Benzyl acetate	$1737-1745 \text{ cm}^{-1}$	υ(C=O)
Dibenzyl ether	$1090-1098 \text{ cm}^{-1}$	v(C-O)
$Cu(acac)_2$	1517-1525 cm <sup>-1</sup>	$\nu(C-C-C)$



**Figure S7** Calibration curves of organic species detected by FTIR during synthesis of copper based nanoparticles: (a) Benzaldehyde at 140 °C, (b) benzyl acetate at 140 °C, (c) benzaldehyde at 140 °C, (d) benzyl acetate at 140 °C and (e) dibenzyl ether at 170 °C. LOD stands for Limit of Detection.

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