Pyridine-Based Low-Temperature Synthesis of CoN, Ni₃N and Cu₃N Nanoparticles

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1. Analytical Equipment

Transmission electron microscopy (TEM). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR)TEM were conducted with a FEI Osiris microscope operating at 200 kV. TEM samples were prepared by evaporating pyridine suspensions on amorphous carbon (Lacey-)film suspended on copper grids. The deposition of the samples on the carbon (Lacey-)film copper grids was performed under argon atmosphere in a glovebox. In the case of copper nitride nanoparticles gold grids were used. Subsequently after preparation the CoN, Ni₃N and Cu₃N samples were slowly heated to 130 °C under vacuum to remove adhered solvent molecules. The grids were thereafter transferred with a suitable vacuum/inert gas transfer module into the transmission electron microscope without any contact to air. Average particle diameters were calculated by statistical evaluation of >100 particles (ImageJ 1.48v).

Dynamic light scattering (DLS) of the redispersed nitride nanoparticles was conducted with pyridine suspensions (1 mg of nanoparticles per 1 ml of pyridine) in quartz cuvettes applying a Nanosizer ZS from Malvern Instruments (U.K.), which was equipped with a laser emitting at 633 nm.

Energy dispersive X-ray spectroscopy (EDXS) was performed with a Bruker Quantax system (XFlash detector). EDX spectra were quantified with the FEI software package "TEM imaging and analysis" (TIA) version 4.7 SP3. Using TIA, element concentrations were calculated on the basis of a refined Kramers' law model, which includes corrections for detector absorption and background subtraction. For this purpose, standard-less quantification, i.e. by means of theoretical sensitivity factors, without thickness correction was applied.

X-ray powder diffraction (XRD). X-ray powder diffraction (XRD) was performed with a STOE STADI-MP diffractometer operating with Ge-monochromatized Cu-K_a-radiation (λ =1.54178 Å). CoN, Ni₃N and Cu₃N samples were diluted with dried glass spheres (9-13 µm, Sigma-Aldrich) to reduce the X-ray absorption of the metal nitride nanoparticles and prepared in glass capillaries under argon. Since the scattering power of the small-sized metal nanoparticles (diameter ≤10 nm) is low, certain non-specific background is observed for all nanoparticles. This nonspecific scattering was fitted by background correction (Win-XPOW, 1.2v).

Rietveld analysis. Whole-diffraction-pattern fitting via Rietveld refinement was applied to verify the crystallite size of the as-prepared CoN and Cu₃N nanoparticles based on XRD data using TOPAS-Academic, v5. Position and integral breadth of each diffraction line were determined after subtracting a linearly interpolated background by fitting a fundamental parameter approach to each individual profile. The volume-averaged crystallite diameters (D_V) were determined by the single-line profile analysis.

Fourier-transform infrared (FT-IR) spectroscopy. Fourier-transform infrared (FT-IR) spectra were recorded with a Vertex 70 FT-IR spectrometer from Bruker Optics. The transmittance of pellets consisting of 300 mg of dried KBr and 0.8 mg of the dried CoN, Ni₃N and Cu₃N nanoparticle sample was measured. A base line correction was applied to diminish the non-specific broad absorption over the full spectral range (4000-400 cm⁻¹) originating from the deep black to brownish colour of the metal nitrides.

Ultraviolet/visible (UV/Vis) spectroscopy. Ultraviolet/visible (UV/Vis) spectra were recorded using a UV-2700 (Shimadzu) equipped with an Ulbricht sphere. Dried Cu_3N samples were measured in reflection as powders (3 mg of sample and 200 mg of dried BaSO₄).

Starting materials. All experiments and purification procedures were performed under inert gas (argon), using standard Schlenk techniques or glove boxes. This also includes all centrifugation and washing procedures. Moreover, sample preparation and sample transfer for analytical characterization were strictly performed under inert conditions, e.g. by using specific transfer modules. Pyridine (ABCR, 99%) was refluxed for three days and freshly distilled over CaH₂. Acetonitrile (Sigma-Aldrich, 99.5%) was refluxed over CaH₂ onto P_4O_{10} and degassed by three freeze-pump-thaw cycles. KNH₂ was synthesized by reacting potassium (Riedel-de-Haën, 99%) in liquid ammonia (Air Liquide, 99.98%) at -78 °C using Fe₂O₃ as a catalyst, followed by filtering and drying *in vacuo*. Cobalt(II)iodide (Sigma-Aldrich, 99%), nickel(II)iodide (Sigma-Aldrich, 99.99%), and copper(I)iodide (Sigma-Aldrich, 99.5%) were used as purchased.

2. Course of the Ammonolysis Reaction

The pyridine-based synthesis strategy follows the well-known mechanism and course of ammonolysis reactions.^[S1] Thus, the formation of CoN, Ni₃N and Cu₃N can be rationalized as discussed for the respective bulk phases.^[S2]

CoN:
$$CoI_2 + K(NH_2) \rightarrow Co(NH_2)_2 + KI$$

 $Co(NH_2)_2 \rightarrow CoN + NH_3\uparrow + H_2\uparrow$
Ni₃N: $NiI_2 + K(NH_2) \rightarrow Ni(NH_2)_2 + KI$
 $Ni(NH_2)_2 \rightarrow Ni(NH) + NH_3\uparrow$
 $3Ni(NH) \rightarrow "Ni_3N_2" + NH_3\uparrow$
 $"Ni_3N_2" \rightarrow Ni_3N + \frac{1}{2}N_2\uparrow$
Cu₃N: $CuI + K(NH_2) \rightarrow Cu(NH_2) + KI$
 $2Cu(NH_2) \rightarrow Cu_2(NH) + NH_3\uparrow$

 $3Cu_2(NH) \rightarrow 2Cu_3N + NH_3\uparrow$

The formation of the amides $Co(NH_2)_2$, $Ni(NH_2)_2$, and $Cu(NH_2)$ is validated by FT-IR spectra of the intermediates showing the characteristic amide-related vibrations $v_{as}(N-H)$, $v_s(N-H)$ and $\delta(NH_2)$. Moreover, a low-energy lattice vibrations are observed (Figure S1).

The transformation of the intermediate amides to the final nitrides CoN, Ni₃N and Cu₃N upon refluxing in pyridine is indicated by characteristic colour changes $Co(NH_2)_2$ (blue) \rightarrow CoN (black), Ni(NH₂)₂ (orange) \rightarrow Ni₃N (black), and Cu(NH₂) (colourless) \rightarrow Cu₃N (red) (Figure S2; see main paper: Figure 1b,c).^[S1,S2a] CoN, Ni₃N and Cu₃N were formed upon completion of the ammonolysis. It is to be noted that the intermediate Ni₃N₂ is known for N₂ release with formation of Ni₃N even at room temperature.^[S1,S2c]

Specific advantages of the novel pyridine-based synthesis strategy relate to the absence of any oxygen source (*viz.* oxide impurities are known to hamper the crystallization), and the use of a moderately coordinating alkaline solvent (i.e. pyridine) that supports the ammonolysis already at low temperatures (i.e. boiling pyridine). All as-prepared nitrides are sensitive to air and moisture, which is illustrated for CoN (Figure S3). Thus, the deep black CoN turned to a reddish colour due to partial hydrolysis at room temperature on a time scale of <5 min.



Figure S1. FT-IR spectra of the amide intermediates: a) $Co(NH_2)_2$, b) $Ni(NH_2)_2$, and c) $Cu(NH_2)$.



Figure S2. Colour change upon transformation of the intermediate amides to the final nitrides in refluxing pyridine: a) $Co(NH_2)_2 \rightarrow CoN$, b) $Ni(NH_2)_2 \rightarrow Ni_3N$, c) $Cu(NH_2) \rightarrow Cu_3N$.



Figure S3. Colour change upon hydrolysis of CoN: a) black colour under argon; b) reddish colour due to partial hydrolysis at room temperature on a time scale of <5 min.

3. Size and Size Distribution

The size distribution and the mean particle diameter of the as-prepared CoN, Ni₃N and Cu₃N nanoparticles were obtained by statistical evaluation of >100 nanoparticles on TEM images (Figure S4; *see main paper: Figure 2*). Accordingly, narrow size distributions were observed. The mean diameters were determined to 4.5 ± 0.7 nm (CoN), 2.7 ± 0.4 nm (Ni₃N), and 4.2 ± 0.7 nm (Cu₃N) (Figure S4).



Figure S4. Diameter and size distribution of CoN, Ni₃N and Cu₃N nanoparticles as obtained by statistical evaluation of >100 nanoparticles on TEM images (*see main paper: Figure 2*).

In addition to TEM analysis, the size distribution was exemplarily also determined for redispersed CoN nanoparticles by dynamic light scattering (DLS). To this concern, the asprepared CoN was centrifuged to remove all dissolved salts and remaining starting materials. Thereafter, the CoN nanoparticles were redispersed with 1 mg of CoN per mL of pyridine. DLS analysis shows a mean hydrodynamic diameter of 5.1 ± 1.3 nm at narrow size distribution (Figure S5). This value is well in agreement with the mean diameter obtained by statistical evaluation of nanoparticles on TEM images (4.5 ± 0.7 nm, Figure S4a).



Figure S5. Particle size distribution obtained via DLS for redispersed CoN nanoparticles in pyridine (1 mg CoN per mL of pyridine).

4. Crystallinity and Chemical Composition

The crystallinity of the as-prepared CoN, Ni₃N and Cu₃N nanoparticles was studied by Xray powder diffraction (XRD) analysis and selective area electron diffraction (SAED) of a large number of nanoparticles (*see main paper: Figure 3*). Azimuthally integrated SAED patterns shown in Figure S6 are comparable with XRD patterns. Accordingly, CoN and Cu₃N turned out as crystalline and are well in accordance to calculated patterns of bulk-CoN and bulk-Cu₃N (Figure S6a,c). Ni₃N, in difference, did not show specific Bragg peaks (Figure S6b).

For the as-prepared crystalline CoN and Cu₃N nanoparticles, Rietveld refinement was performed to deduce the crystallite diameter (Figure S7). As a result, volume-averaged crystallite diameters (D_V) of 4.6 nm (CoN) and 4.2 nm (Cu₃N) were determined. These values

are well in agreement with the particle diameter obtained via statistical evaluation of particles on TEM images (Figure S4; *main paper: Figure 2*).



Figure S6. Azimuthally integrated diffracted intensity of SAED patterns (*see main paper: Figure 3a,c,e*) of the as-prepared CoN, Ni₃N and Cu₃N nanoparticles plotted as a function of the spatial frequency 1/d (references: ICDD-No. 01-080-6770 (CoN); ICDD-No. 01-070-9598 (Ni₃N); ICDD-No. 00-047-1088 (Cu₃N)).



Figure S7. Rietveld refinement of the as-prepared crystalline CoN and Cu₃N nanoparticles.

The as-prepared nitride nanoparticles (i.e. subsequent to refluxing in pyridine) were investigated by FT-IR spectroscopy and show the characteristic vibrations of pyridine attached to the surface of the nanoparticles (Figure S8a,c,e; *see main paper: Figure 4a*). After purification with acetonitrile at room temperature (i.e. three times redispersion/centrifugation in/from acetonitrile followed by drying in vacuum), however, FT-IR spectra show weak vibrations related to pyridine as a surface conditioning. Moreover, the completeness of the ammonolysis (i.e. absence of amides and imides) and the absence of any hydrolyzation (i.e. absence of hydroxides) are evidenced (Figure S8b,d,f; *see main paper: Figure 4b*).



Figure S8. FT-IR spectra of CoN, Ni_3N and Cu_3N nanoparticles subsequent to synthesis in refluxing pyridine (a,c,e) as well as after washing by redispersion and centrifugation from acetonitrile (b,d,f).

The chemical analysis of particle agglomerates obtained by EDXS in a transmission electron microscope was performed by the quantification of the N-*K* and the Co/Ni/Cu-*K* lines (Figure S9: red frame; Table S1). EDXS also show characteristic X-ray lines of carbon (C- $K_{\alpha l}$ line) and Cu (Cu-*L* series) arising from the supporting substrate which consists of a thin amorphous carbon film suspended on a Cu grid. Low amounts of oxygen, silicon, and fluorine originate from substrate contaminations, as indicated by the background spectra that were separately recorded on the bare substrate in a region near the particles.



Figure S9. EDXS area scans of the as-prepared CoN (a), Ni_3N (b) and Cu_3N (c) nanoparticles. The element mapping in the red frame was used to determine the respective composition (Table S1).

Table S1 Chemical composition of the as-prepared CoN, Ni_3N and Cu_3N nanoparticles according to EA and EDXS area scans (in at-%).

		С	Η	Ν	Μ	M/N
					(Co,Cu,Ni)	
CoN	EA	8.2	36.5	27.9	27.1	1.0
	EDXS	/	/	49.7	50.3	1.0
Ni ₃ N	EA	9.6	23.2	16.8	50.4	3.0
	EDXS	/	/	25.3	74.7	3.0
Cu ₃ N	EA	7.5	17.0	18.4	57.1	3.1
	EDXS	/	/	25.0	75.0	3.0

5. Optical Properties and Band Gap

The optical band gap of the as-prepared Cu₃N was determined based on the optical spectra by applying the Kubelka-Munk approach and via a Tauc plot (Figure S10; *see main paper: Figure 5d*). Accordingly, a direct band gap with 2.0 eV was determined.



Figure S10. Tauc plot based on the UV-Vis spectrum of the as-prepared Cu₃N (*see main paper: Figure 5d*).

References

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