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# Solid-State C–S Coupling in Nickel Organochalcogenide Frameworks as a Route to Hierarchical Structure Transfer to Binary Nanomaterials

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different binary Ni-based nanomaterials via selective coupling of organic units was developed. We suggested the use of substituted aryl groups in organosulfur ligands (SAr) as traceless structure-inducing units to prepare nanostructured materials. At the first step, it was shown that the slight variation of the type of SAr units and synthetic procedures allowed us to obtain nickel thiolates  $[Ni(SAr)_2]_n$  with diverse morphologies after a self-assembly process in solution. This feature opened the way for the synthesis of different nanomaterials from a single type of precursor using the



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phenomenon of direct transfer of morphology. This study revealed that various nickel thiolates undergo selective C–S coupling under high-temperature conditions with the formation of highly demanding nanostructured NiS particles and corresponding diaryl sulfides. The *in situ* oxidation of the formed nickel sulfide in the case of reaction in an air atmosphere provided another type of valuable nanomaterial, nickel oxide. The high selectivity of the transformation allowed the preservation of the initial organochalcogenide morphologies in the resulting products.

# INTRODUCTION

Nanostructured inorganic architectures on the basis of transition metal sulfides made an outstanding contribution to materials science. Their unique electronic properties and wide possibilities for tuning the morphology and composition of nanocrystals allowed the creation of efficient photo- and electrocatalysts,<sup>1,2</sup> energy storage materials,<sup>3</sup> sensors and biological labels,<sup>4-6</sup> light-emitting devices,<sup>7-10</sup> room-temperature ferromagnetics,<sup>11</sup> and high-capacity materials for lithium, sodium, and magnesium ion batteries.<sup>12–14</sup>

Introduction of organic moieties in the transition metal sulfides opened up new horizons for the preparation of functional materials. For example, the high redox activity of organic dithiolato ligands attached to the transition metal atoms can be employed in the production of hydrogen via photocatalytic hydrogen evolution reaction.<sup>15</sup> Metal clusters with thiolate ligands are promising materials for optoelectronic and photovoltaic devices.<sup>16</sup> Polymeric thiolate structures based on transition metal units bound by organic sulfur-containing bridges not only possessed pronounced band-like electronic properties<sup>17</sup> but also demonstrated excellent performance in catalytic C–S cross-coupling reactions<sup>18,19</sup> and heterofunctionalization of unsaturated carbon–carbon bonds,<sup>20–22</sup> which form the base of modern organosulfur chemistry.<sup>23–27</sup> The key feature associated with the structure of polymeric thiolates is the high affinity of sulfur atoms for metal centers and the

stability of the metal–sulfur core, which makes the synthesis of these compounds simple and easily reproducible. However, chemical transformations involving coordination polymers of metal thiolates usually proceed on defects or low-coordination surface sites<sup>21,22</sup> and often include leaching of small thiolate species in solution.<sup>18–20</sup> Therefore, the preferable manner of core group activation is destruction of polymeric structure, which seriously complicates the modification of these materials without alteration of their micro- and nanoscale properties.

Previously published papers devoted to the synthesis of nickel thiolates<sup>18,28</sup> have outlined the general tendencies in the synthesis of nanostructured coordination polymers. It was shown that the nature of the substituents in the organic groups of nickel thiolates was responsible for the size and shape of the resulting thiolate particles. At the same time, the question about the possibility of preparing coordination polymers with the same composition and different structures was only slightly elucidated. Therefore, during the first step of this study, we decided to optimize the nickel thiolate synthesis conditions

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and to find the possible ways to prepare particles with different morphologies.

In this work, we describe the high-temperature solid-state C-S coupling reaction in nickel thiolate coordination polymers  $[Ni(SAr)_2]_n$ , which opened the way for the direct transfer of morphology from nickel thiolates to different nickelbased nanomaterials during temperature-induced modification. It was revealed that under an inert atmosphere at temperatures of approximately 300-700 °C, nickel thiolates selectively decompose with the formation of corresponding diaryl sulfide and nanosized nickel sulfide. Tuning of the reaction atmosphere allows us to widen the scope of the transformation. Nanosized nickel oxide can be readily synthesized from  $[Ni(SAr)_2]_n$  under an air atmosphere by *in situ* oxidation of the formed nickel sulfide. Retention of the initial thiolate morphologies in the resulting nickel-containing particles clearly demonstrates the preservation of the Ni-S core structure during the C-S coupling. The studies of temperature-induced reactions were preceded with the optimization of the nickel thiolate preparation method, which allowed us to propose the general procedure for the preparation of nanomaterials with different morphologies from a single set of reagents. The discovered process opened the way for selective modification of sulfur-containing metal-organic architectures and formed the basis for the new method for the synthesis of structurally defined nickel oxides and sulfides, which can find numerous applications in the production of solar cells, batteries, supercapacitors, and catalysts.<sup>29-35</sup>

# RESULTS AND DISCUSSION

To choose the appropriate model system for the reaction optimization, a number of nickel thiolates were synthesized and subjected to X-ray powder diffraction analysis (XRD) to find the structures with the highest order among the prepared particles. The desired compounds were obtained by the reaction of nickel acetylacetonate with the corresponding thiol in solution (Scheme 1). The studied sequential trans-

Scheme 1. Stepwise Formation of Nickel Thiolate Particles from Soluble Nickel Salt and the Corresponding Aromatic Thiol



formations included ligand substitution, polymeric chain growth, and assembly of nanostructured materials, which resulted in all cases in the formation of solid products with almost quantitative yields. The morphologies of the isolated particles were fully consistent with the published data.<sup>18</sup>

After the synthesis, nickel-containing coordination polymers were analyzed by XRD, which demonstrated the considerable variations in the crystallinity and degree of ordering for the compounds with different substituents in the aromatic rings (Figure 1).

In the case of the unsubstituted nickel thiophenolate, the XRD pattern consisted of several broad peaks, which indicated the formation of a highly dispersed phase. Highly ordered structures featured by several narrow intense peaks in diffractogtams were detected for p-NH2- and p-Cl-substituted thiolates. In the first case, the high crystallinity was caused by additional coordination of amino groups to nickel atoms upon formation of the framework. The formation of the same ordered structure in the case of the *p*-Cl-substituted compound clearly demonstrated that the chains of coordination polymers can form such structures even in the absence of strongly coordinating atoms. In contrast, the change of the p-Cl substituent to p-Br and the p-NH<sub>2</sub> group to p-OH led to the formation of the mixture of different phases that make obtained materials less promising as starting compounds for the synthesis of nanostructured architectures. Comparison of the XRD patterns for nickel thiolates with the XRD pattern for crystalline Ni(acac)<sub>2</sub> clearly demonstrated the complete conversion of the starting material in all cases. On the basis of diffraction data and previously published electron microscopy measurements,<sup>18</sup> the nickel thiolate with p-Cl groups in the aromatic rings was chosen as a model compound for the optimization of the synthesis conditions.

In the model system,  $[Ni(S-p-ClC_6H_4)_2]_n$  was prepared from the nickel acetylacetonate and the corresponding thiol with the use of different solvents and thiol loadings (Table 1). All reactions were carried out at room temperature.

During the first step of optimization, the different quantities of thiol were used for the reaction to determine the ratio between the nickel precursor and the thiol required for the preparation of nickel thiolate with a high yield and a regular morphology. The stoichiometric ratio (1:2) and 1:3 and 1:5 thiol loadings were employed (Table 1, entries 1-3, respectively). In all cases, the reaction proceeded smoothly and the product with the desired morphology was obtained, which was verified by electron microscopy (see Figures S1-S6); however, an at least 1.5-fold excess of thiol was required to reach product yields of approximately 90-95%. The right choice of solvent usually plays an important role in the synthesis of nanostructured materials, because the nature of the medium determines the stability of the disperse phase in the colloidal system and controls the regularities of growth and self-assembly at the solid-liquid interface. The screening of solvents in the studied synthesis of nanostructured materials revealed the key role of the medium in the nickel-containing species assembly. The best yields of the product (78-95%) were obtained with the use of low-polar organic solvents (Table 1, entries 3-5), and a comparable reaction system efficiency was observed in the case of some oxygen-containing liquids like THF, ethyl acetate, and methanol (Table 1, entries 6-8, respectively). Application of nonpolar hydrocarbons like toluene allowed us to isolate the product in satisfactory 57% yield (Table 1, entry 9), whereas the use of DMF, DMSO, or acetonitrile resulted in poor thiolate yields of <40% (Table 1, entries 10-12). It is worth mentioning that regardless of the nature of employed media the substitution reactions between nickel acetylacetonate and thiol took place immediately after mixing of the reagents, but at the same time, the rate of selfassembly of soluble particles differed notably. This feature of the employed system was responsible not only for the product yield but also for the synthesized particle morphology, which



**Figure 1.** X-ray powder diffraction data for nickel thiolates  $[Ni(SAr)_2]_n$  with different substituents in the aromatic rings. The diffractogram of the  $Ni(acac)_2$  control sample is also provided.

Table 1. Optimization of the Conditi	ions for Nickel Thiolate
Nanostructured Material Synthesis	

$Ni(acac)_2 + CI \xrightarrow{SH} SH \xrightarrow{Solvent} [Ni(Sp-CIC_6H_4)_2]_n$			
entry	Ni(acac) <sub>2</sub> :ArSH	solvent	yield <sup>a</sup> (%)
1	1:2	$CH_2Cl_2$	79
2	1:3	$CH_2Cl_2$	91
3	1:5	$CH_2Cl_2$	95
4	1:5	DCE	82
5	1:5	CHCl <sub>3</sub>	78
6	1:5	THF	78
7	1:5	ethyl acetate	76
8	1:5	CH <sub>3</sub> OH	68
9	1:5	toluene	57
10	1:5	DMF	39
11	1:5	DMSO	20
12	1:5	CH <sub>3</sub> CN	3
<sup><i>a</i></sup> Based on the weight of the isolated precipitate.			

was clearly shown by electron microscopy (SEM) analysis of the prepared materials (Figure 2).

Particles isolated from chlorinated solvents and tetrahydrofuran appeared as well-ordered microsized aggregates of nanoscale two-dimensional nickel thiolate sheets. The size of aggregates varied in the range of 5–10  $\mu$ m, and the type of aggregation was determined by the nature of the solvent. Meshy structures with the minor amount of lamellar inclusions were detected in the case of methylene chloride (Figure 2A). The stacks forming biconcave microparticles were obtained after the reaction in chloroform (Figure 2B). Synthesis in 1,2dichloroethane (DCE) resulted in fan-shaped aggregates (Figure 2C). Holey round-shaped particles precipitated from the tetrahydrofuran (Figure 2D). The microcrystalline product with the size of individual crystals of  $\sim 1 \,\mu m$  was formed in the case of the use of DMSO as a solvent (Figure 2E). Dense aggregates without a specific morphology were obtained in DMF, acetonitrile, and methanol (Figure 2F). For other solvents, the mixtures of particles with different morphologies

were detected by electron microscopy. SEM measurements were supplemented by X-ray powder diffraction studies to analyze the phase composition of the prepared materials. Analysis of the obtained XRD patterns (see Figure S7) showed that the samples isolated from chlorinated solvents had a similar phase composition, but in some other cases (for example, in the case of tetrahydrofuran and DMSO), the notable amounts of impurities were detected along with the main phase. Therefore, as a summary of the findings described above, the synthesis in chlorinated solvents is the most promising method for the preparation of nickel thiolates because it allows the preparation of the well-structured materials with high yields and purities.

In the next step, the chemical properties of prepared coordination polymers were studied with an eye on the synthesis of nickel-containing nanostructured materials using thiolate particles as a template. The emphasis was placed on the development of selective methods for temperature-induced modification in the solid phase. For the evaluation of the optimal reaction conditions, a number of nickel thiolates synthesized from Ni(acac)<sub>2</sub> in  $CH_2Cl_2$  were subjected to thermogravimetric analysis (TGA), which has revealed the features of the behavior of the prepared materials at temperatures of ≤1200 °C in an argon atmosphere. The first derivatives of TGA curves clearly reflected the difference in the rate of nickel thiolate decomposition and in the temperature profiles of the reactions depending on the nature of substituents in the aromatic rings (Figure 3A). In the case of the unsubstituted thiophenolate, the reaction took place at a relatively low temperature and had the highest rate among all carried out processes. The maximum rate was observed at 273 °C. It can be explained by the high volatility of the organic products of the reaction, which can be easily removed from the reaction mixture even upon moderate heating. In the presence of heavier substituents in organic fragments of nickel coordination polymers, an increase in decomposition temperature was observed. Therefore, the maximum decomposition rate was observed at 309 or 375 °C for p-Cl- or p-OHsubstituted thiolates, respectively. The profiles of the differ-



Figure 2. SEM images of the  $[Ni(S-p-ClC_6H_4)_2]_n$  particles prepared in different solvents: (A)  $CH_2Cl_2$ , (B)  $CHCl_3$ , (C) DCE, (D) THF, (E) DMSO, and (F)  $CH_3OH$ .



Figure 3. (A) DTG curves for nickel thiolates with various substituents in aromatic rings. (B, C) Energy dispersive X-ray (EDX) spectra for the initial nickel thiolates (colored blue) and samples after TGA (colored red) in the case of thiolates containing (B) *p*-Br and (C) *p*-Cl substituents.

ential TG (DTG) curves in the case of these substituents were similar to the DTG curves for nickel thiophenolate, although their broadening and the appearance of additional features were observed, which indicates the stepwise removal of organic residues. This effect was especially pronounced in the case of the *p*-Br-substituted compound. The DTG curve for this sample contained a series of extrema in a wide temperature range from 100 to 700  $^{\circ}$ C. A similar multistage decomposition

is observed in the case of the amino group as a substituent. To establish the changes in the chemical composition of nickel thiolates after thermal treatment, samples were analyzed before and after TGA using the X-ray microanalysis technique (EDX), which showed an increase in the weight fraction of sulfur and nickel in the sample, which suggests that nickel sulfide is predominantly formed as a decomposition product of nickel thiolates in an inert atmosphere. A comparison of the spectra of the initial nickel thiolates containing p-Br and p-Cl substituents with the spectra of their decomposition products allowed one to conclude that the organic fragments were completely removed during the thiolate treatment. Peaks corresponding to bromine and chlorine atoms, for example, in benzene rings, were not observed in the spectra of the treated samples, although they were present as intense peaks in the spectra of the initial coordination polymers with *p*-Br (Figure 3B) and p-Cl (Figure 3C) substituents. Thus, as a result of TGA, the key information was obtained for the creation of temperature programs for the scaling of nickel thiolate conversion.

On the basis of TGA data, the optimal temperature programs were proposed for the further study of the process. For the reaction in an argon atmosphere, the working temperature was chosen to match the conditions required for almost all studied materials except strongly deviating nickel thiolate with a *p*-Br substituent. Therefore, in the general procedure reactions were carried out at 500 °C; for  $[Ni(S-p-BrC_6H_4)_2]_n$ , the temperature was increased to 800 °C (Scheme 2). At the same time, starting from 200 °C, the heating rate

Scheme 2. Temperature-Induced Modification of Nickel Thiolates in an Argon or an Air Atmosphere $^{a}$ 



"The main products proposed on the basis of X-ray microanalysis are shown. The weight loss percentage is provided for each experiment. The theoretical weight loss percentage (calculated for NiS or NiO formation in the reaction in an argon or air atmosphere, respectively) is given in parentheses.

was slowed to exclude the distortion of the structure of the resulting materials during the rapid decomposition of nickel thiolates. As in the case of the TGA experiment, calculations based on the material weight loss (Scheme 2) as well as X-ray microanalysis of the obtained samples (see Figures S8–S12) confirmed the formation of nickel sulfide, which, however, contained notable amounts of oxidized NiS<sub>x</sub>O<sub>y</sub> species due to the reaction of the product surface with oxygen impurities in the reaction chamber or due to product degradation during the storage.

The facile oxidation of thiolate decomposition products even with oxygen traces inspired us to modify the procedure and to carry out the reaction in air to spread the proposed methodology on the synthesis of nanosized nickel oxide. Synthesis was performed in the air flow at different temperatures from 600 to 800 °C (Scheme 2). All reactions proceeded smoothly with the formation of NiO as a main product, which was confirmed by X-ray microanalysis (see Figures S13–S19) and comparison of practical and theoretical weight losses (Scheme 2). However, the use of relatively low reaction temperatures led to the appearance of the sulfide product in the obtained material. In the case of  $[Ni(S-p-ClC_6H_4)_2]_n$  at 600 °C, approximately 2–3% of NiS was formed as a side product. The quantity of the impurities can be decreased to trace amounts of <1% by increasing the temperature to 700–800 °C (see Figures S13–S15). It is important to mention that for all temperatures the mass loss values for  $[Ni(S-p-ClC_6H_4)_2]_n$  were almost identical and perfectly matched the theoretical value (Scheme 2).

To establish the main reaction pathway leading to the formation of nickel sulfide from nickel thiolate coordination polymers in an inert atmosphere, GC-MS analysis of the products deposited from the gas phase after the thermal decomposition of  $[Ni(SAr)_2]_n$  particles was carried out. For all tested compounds, the formation of the corresponding diaryl sulfide Ar<sub>2</sub>S via C-S coupling was observed. In the case of unsubstituted nickel thiophenolate and nickel thiolates with p-Cl and *p*-NH<sub>2</sub> substituents, the disulfide product was the only organic compound detected in a notable amount (see Figures S20–S25). The picture was more complicated for the thiolate bearing p-OH groups. As in the previous cases, two organic groups in thiolate underwent C-S coupling, which expectedly gave the diaryl sulfide product; however, the simultaneous appearance of phenol and 4-mercaptophenol was clearly shown by GC-MS (see Figures S26-S29). Possibly, after C-S coupling, under high-temperature conditions the free phenolic moieties partially reduced the carbon-sulfur bonds in the product with formation of new aromatic species. The increase in the reaction temperature to 800 °C in the case of p-Brsubstituted nickel thiolate led to the facile cleavage of carbonsulfur and carbon-bromine bonds and the appearance in addition to diaryl sulfide of a few more initially unexpected organic products as 1,4-dibromobenzene and 4'-bromo-4mercaptobiphenyl (see Figures S30-S33). On the basis of the observations made, one can conclude that despite the existence of some side transformations, the solid-phase C-S coupling is a predominant process occurring during nickel thiolate thermal treatment, which is in excellent agreement with the formal stoichiometry of the reaction.

The morphology of the solid materials obtained in an argon atmosphere was examined by SEM, which has shown that the most promising regular structures were formed from [Ni(S-p- $ClC_6H_4)_2]_n$  as a starting compound (Figure 4A). The homogeneous structure with no specific morphology was formed in the case of unsubstituted nickel thiophenolate; in the case of *p*-Br-substituted thiolate, the need to increase the reaction temperature to 800 °C led to the partial melting of the product and, accordingly, to the loss of the initial structure (see Figure S34). Due to the removal of organic fragments from the particles of nickel thiolates, their size decreased, on average, from 500 to 200-300 nm in the case of nickel thiophenolate (see Figure S34) and from 10–20 to 5–10  $\mu$ m in the case of p-Cl-substituted nickel thiolate (Figure 4A). It is noteworthy that in both cases, after the reaction the microparticles showed a clearly defined nanostructure, which was not typical for the initial thiolates. From the SEM data, one can clearly see the structural subunit of the prepared nanoparticles with a size of



**Figure 4.** SEM images of the nanomaterials obtained after temperature-induced modification of nickel thiolate  $[Ni(S-p-ClC_6H_4)_2]_n$  in (A) an argon atmosphere at 500 °C and in an air atmosphere at (B) 600 °C and (C) 800 °C. XPS spectra in the Ni  $2p_{3/2}$  region for the corresponding nickel-based nanomaterials (D–F, respectively).

approximately 20-30 nm. The porous material was synthesized from a hydroxy-substituted nickel coordination polymer; however, a high degree of aggregation of particles in the starting compound led to their sticking in the final product with formation of the sponge with an irregular structure. Upon conversion of the amino-substituted compound, the surface of the obtained material was notably smoothed, perhaps, by minor amounts of nonvolatile organic side products (see Figure S35). Electron microscopy analysis of the materials synthesized in an air flow revealed the trends in the nickel thiolate particles morphology alteration during the reaction under oxidative conditions. The microlevel morphology of the particles prepared from p-Cl- and p-Br-substituted nickel thiolates was generally preserved. The average size of the particles was approximately 5–10  $\mu$ m for nickel oxide prepared from *p*-Cl-substituted nickel thiolate at 600 °C (Figure 4B), 700 °C (see Figure S36), and 800 °C (Figure 4C) and  $2-4 \,\mu m$ for NiO prepared from  $[Ni(S-p-BrC_6H_4)_2]_n$  at 800 °C (see Figure S37). The synthesis at a relatively low temperature of 600 °C led to the appearance of the nanostructure of the product with a subunit size of approximately 20-30 nm. Reactions at higher temperatures resulted in the increase in subunit size due to the coalescence of the formed nickelcontaining species. At 700 °C, this parameter reached 30-50 nm and at 800 °C increased to several hundreds of nanometers. Large particles reflecting the initial crystalline structure were detected in the case of  $[Ni(S-p-NH_2C_6H_4)_2]_n$  thermolysis at 800 °C (see Figure S37). Nevertheless, these particles consisted of well-ordered subunits with sizes of approximately 50–200 nm. The thermal treatment of nickel thiophenolate and *p*-OH-substituted nickel thiolate at the same temperature resulted in the formation of poorly ordered materials with less expressed nanostructure (see Figure S38).

To determine the chemical state of nickel atoms in the resulting products, the prepared materials were analyzed by Xray photoelectron spectroscopy (XPS). The typical spectrum for nanomaterials synthesized in an inert argon atmosphere consisted of three peaks in the Ni  $2p_{3/2}$  region (Figure 4D; see also Figures S39–S41). According to the literature data,<sup>36–38</sup> the main peaks observed at 853.1-853.3 eV as well as small satellites that appeared at 860.3-860.9 eV were attributed to the nickel sulfide. In addition to NiS, the partially oxidized form of this material was detected on the sample surface. The values of Ni 2p3/2 binding energies for oxygen-containing species were 855.2-855.5 eV, which allowed us to propose their sulfate-like structure<sup>36</sup> with a formal elemental composition of  $NiS_xO_y$ . It is important to mention that the appearance of this type of impurities on the surface is common for the nickel sulfide nanomaterials exposed to an air atmosphere.<sup>38</sup> XPS data for the products prepared in an air

# Scheme 3. Developed Approach for the Hierarchical Structure Transfer to Ni-Based Binary Nanomaterials<sup>a</sup>



 $a^{\prime}(A)$  Synthesis of the nickel thiolate template with a unique morphology stabilized and controlled by organic SAr groups. (B) Structure transfer to binary nanomaterials via C–S coupling reaction accompanied by (C) formation of aryl sulfide, which can be recycled.

atmosphere at 600 °C (Figure 4E) and 800 °C (Figure 4F, see also Figures S42–S45) confirmed the formation of nickel oxide as it was proposed on the basis of EDX analysis and weight loss measurements. In all cases, the XPS spectra in the Ni  $2p_{3/2}$ region had a complex structure with three main lines. The pairs of peaks at 853.7-853.9 and 855.4-855.8 eV were attributed to the split Ni  $2p_{3/2}$  line of NiO, whereas the latter components with maxima at 860.8-861.2 and 862.1-866.3 eV (low-intensity component) were assigned to the Ni  $2p_{3/2}$ satellite of NiO.<sup>36,39,40</sup> It is important to mention that the fine structure of the typical nickel oxide XPS spectrum can be even more complicated, and a number of additional components can be extracted during precise fitting.<sup>39</sup> As a result of the current stage, the scope of the reaction was expanded to nanosized nickel oxide synthesis with a slight modification of the experimental procedure.

Taking into account the foregoing, one can conclude that nickel thiolates  $[Ni(SAr)_2]_n$  with different *p*-substituents can be used as precursors and templates for the preparation of nickel-containing binary nanomaterials. It is essentially in this context that the variation of the substituent can significantly change the morphology of the initial thiolate and final product. For example, unsubstituted nickel thiophenolate and nickel thiolate with hydroxyl groups appeared as aggregates of small particles without a specific shape. These compounds were readily transformed to the nanosized binary materials, which, however, had only one level of organization in full accordance with the stated principle of morphology transfer. The similar behavior was observed for the p-NH2-substituted nickel thiolate. Additional coordination of amino groups to nickel atoms allowed generation of the coordination polymer with more regular structure, but no extra structural levels were created at microscale; therefore, the morphology transfer resulted in the formation of simply aggregated nanosized particles. The picture was completely different in the case of halogen-containing nickel thiolates, which can be characterized as compounds with an easily tunable and diverse morphology. The use of these compounds for annealing opened the way for the creation of nanomaterials with a complex hierarchical structure, which was the main goal of this study. Possibly, electron-withdrawing properties of chlorine and bromine substituents driving the charge redistribution in the aromatic rings as well as their potential for additional coordination contribute to noncovalent interactions of the  $\pi-\pi$  stacking type between aromatic moieties, which stabilize the hierarchical structure of nickel thiolates.

The substituent effect was further studied on an additional set of nickel thiolates. First, the influence of the substituent position in the aromatic rings on the morphology of nickel thiolates was evaluated. For this purpose, thiolates with o-Cl, m-Cl, o-Br, and m-Br substituents were synthesized and their morphology was studied by electron microscopy (see Figure S46) and compared with the morphology of p-substituted analogues. It was established that a strong steric effect resulted in the complete disappearance of regular structure in the case of *o*-substituted thiolates and a notable morphology alteration in the case of *m*-substituted thiolates. The formation of aggregated flakes with sizes of approximately 1  $\mu$ m was detected for  $[Ni(S-m-ClC_6H_4)_2]_n$ , and in the case of  $[Ni(S-m-ClC_6H_4)_2]_n$  $BrC_6H_4)_2]_n$ , small particles approximately 100-300 nm in diameter were observed. Therefore, the spatial arrangement of substituents is an important factor that is responsible for the thiolate hierarchical structure stabilization. An interesting observation was made for the nickel thiolate synthesized from 2-aminothiophenol. The resulting compound appeared as submicrocrystalline powder with individual crystal sizes approximately 200-300 nm (see Figure S46) and had a light yellow-green color atypical for  $[Ni(SAr)_2]_n$  coordination polymers. The prepared material was characterized earlier by X-ray absorption spectrocsopy,<sup>18</sup> and its properties can be explained by formation of a monomeric crystalline complex with a chelating SAr ligand. Finally, two dithiols, 1,4benzenedithiol and 4,4'-dimercaptobiphenyl, were used for nickel thiolate synthesis. Depending on the ligand structure, two completely different types of morphology were observed (see Figure S46). Particles obtained with the use of 1,4benzenedithiol had diameters of approximately 50-100 nm and were merged into 500-700 nm aggregates. In contrast, synthesis on the basis of 4,4'-dimercaptobiphenyl gave perfectly shaped spherical particles with diameters of 300-400 nm. It is noteworthy that the Ni:S ratio determined by EDX analysis (see Figures S47 and S48) was approximately 1:4

for thiolate prepared form 1,4-benzenedithiol and approximately 1:3 for thiolate prepared form 4,4'-dimercaptobiphenyl, which indicated the passive role of the second sulfur atom in the association of the Ni(SAr)<sub>2</sub> units in the first case and partial implementation of linker-type behavior of sulfurcontaining ligands in the second case. It is worth mentioning that the latter type of growth favored the formation of particles with a regular morphology. All synthesized thiolates were used as starting materials for annealing in an air atmosphere at 800 °C. The reaction proceeded smoothly with the formation of aggregated nickel oxide particles with average sizes of approximately 100-200 nm, which was demonstrated by electron microscopy (see Figure S49) and X-ray microanalysis (see Figures S50-S56). No strong correlations between structures of initial thiolates and prepared NiO particles were observed. Thereby, the crucial role in the formation of stable and tunable hierarchical structure of nickel thiolate, which can be easily transferred to binary nanomaterials, is played by noncovalent interactions between aromatic moieties. These forces can be adjusted by variation of the initial synthesis conditions of the materials. At the same time, they are strong enough to form the unique structure of the coordination polymer and particularly the Ni-S core, and the spatial separation of core atoms and side aromatic groups allows the removal of organic substituents without initial morphology distortion.

# CONCLUSIONS

In summary, the new solid-phase C-S bond formation reaction involving metal-containing coordination polymers was found to be an efficient route for the synthesis of nickelbased nanomaterials via direct hierarchical structure transfer (Scheme 3). The desired morphology can be achieved on the initial step of the synthesis of nickel thiolate coordination polymers by a change in the substituent in the organic ligands of thiolate or by the choice of the solvent, which has a pronounced effect on the morphology of the particles grown from initially formed soluble species (Scheme 3, step A). Temperature-induced selective conversion of nickel thiolates in an inert atmosphere led to the exclusive formation of nanosized nickel sulfide and the corresponding diaryl sulfide. The switch from an inert to a reactive gas atmosphere allows the product composition to be changed selectively. Introduction of oxygen into the reaction system led to the formation of nickel oxide instead of nickel sulfide. The key feature of the process is the preservation of the initial thiolate particle morphology in the final product, which makes possible the creation of different well-ordered assemblies of nickelcontaining nanoparticles by tuning nickel thiolate synthesis conditions (Scheme 3, step B). The organic diaryl sulfide product detected in the reaction in an inert atmosphere can be used itself as a valuable  $compound^{23-25}$  or reduced to the corresponding thiol<sup>41,42</sup> for further application in the next cycle of metal thiolate synthesis (Scheme 3, step C).

Overall, here we suggest an efficient procedure for generating a variety of new metal organochalcogenide morphologies by tuning the molecular level cooperative effect of organic substituents at the sulfur atom, followed by removal of organic substituents and transfer of hierarchical structure to form nanostructured nickel sulfides and oxides. Thus, organic sulfides play the role of traceless structure-inducing groups. In the case of highly valuable nanostructured nickel sulfides, organic thiolates can be regenerated and reused again. We anticipate that the approach developed here can also be used to prepare a number of other metal chalcogenides.

# EXPERIMENTAL SECTION

**General Considerations.** Nickel acetylacetonate, thiophenol, substituted aromatic thiols, and all used solvents were purchased from commercial sources.

X-ray powder diffraction (XRPD) studies were carried out at the Xray structural analysis beamline (XSA)<sup>43</sup> of the Kurchatov Synchrotron Radiation Source (National Research Center Kurchatov Institute) with the use of monochromatic radiation with a wavelength of 0.8 Å (photon energy of 15498 eV). The two-dimensional diffraction patterns were collected by a Rayonix SX165 detector and further integrated into the standard form of  $I(2\theta)$  dependence using Dionis software.<sup>44</sup>

XPS spectra were recorded on an ESCA unit of the NanoPES beamline of the Kurchatov Synchrotron Radiation Source (National Research Center Kurchatov Institute) equipped with a high-resolution SPECS Phoibos 150 hemispherical electron energy analyzer with a monochromatic Al X-ray source (excitation energy of 1486.61 eV;  $\Delta E = 0.2$  eV).

Thermogravimetric analysis was performed on a Shimadzu DTG-60H analyzer. The measurements were carried out in an argon atmosphere within the temperature range of 40-1200 °C. The heating rate was 20 °C/min.

Organic products of the reactions were identified by GC-MS with the use of an Agilent Technologies 6890B gas chromatograph (HP-5 ms column) equipped with mass-selective detector MSD 5975; before the measurements, samples were dissolved in dichloromethane.

For the SEM measurements, the samples were glued to the surface of a 1 in. aluminum specimen stub by conductive carbon-based plasticine and coated by a 15 nm layer of carbon. The observations were carried out using a Hitachi SU8000 field-emission scanning electron microscope (FE-SEM). Images were acquired in secondary electron mode at a 2 or 10 kV accelerating voltage. X-ray microanalysis (EDS-SEM) was performed with the use of an Oxford Instruments X-max 80 energy dispersive X-ray spectrometer at a 20 kV accelerating voltage.

Synthesis of  $[Ni(S-p-ClC_6H_4)_2]_n$  with Different Thiol Loadings. First, 7.7 mg (0.03 mmol) of Ni(acac)\_2 was dissolved in 0.5 mL of dichloromethane and mixed with 0.5 mL of a 4-chlorothiophenol solution (0.06, 0.09, or 0.15 mmol of thiol) in dichloromethane. The reaction mixture was kept at room temperature for 15 min until the product had completely precipitated. The resulting solid nickel thiolate was separated by centrifugation, washed with dichloromethane (3 × 4 mL), and dried under reduced pressure at room temperature. For the additional experiments devoted to the study of nickel thiolate properties, the selected procedure was scaled up to 1.5 mmol of Ni(acac)\_2 loading (see Scaled Procedure for the Synthesis of Nickel Thiolates).

**Synthesis of** [Ni(S-*p*-ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>]<sub>*n*</sub> in Different Solvents. First, 7.7 mg (0.03 mmol) of Ni(acac)<sub>2</sub> was dissolved in 0.5 mL of the desired solvent (acetonitrile, toluene, THF, methanol, DMSO, DMF, ethyl acetate, 1,2-dichloroethane, or chloroform) and mixed with 0.5 mL of a 4-chlorothiophenol solution (21.7 mg, 0.15 mmol of thiol) in the same solvent. The reaction mixture was kept at room temperature for 15 min until the product had completely precipitated. The resulting solid nickel thiolate was separated by centrifugation, washed with chloroform (3 × 4 mL), and dried under reduced pressure at room temperature. For the additional experiments devoted to the study of nickel thiolate properties, the selected procedure was scaled up to 1.5 mmol of Ni(acac)<sub>2</sub> loading (see Scaled Procedure for the Synthesis of Nickel Thiolates).

Scaled Procedure for the Synthesis of Nickel Thiolates. First, 385.4 mg (1.5 mmol) of Ni $(acac)_2$  was dissolved in 6 mL of the desired solvent and mixed with 7.5 mmol of thiol (neat liquid for liquid thiols or 6 mL of the chosen solvent for solid thiols). The reaction mixture was kept at room temperature for 30 min until the product had completely precipitated. The resulting solid nickel

thiolate was separated by centrifugation, washed with dichloromethane (5  $\times$  10 mL), and dried under reduced pressure at room temperature.

Thermal Decomposition of Nickel Thiolates under an Argon Atmosphere. Twenty milligrams of nickel thiolate was placed in a quartz boat and transferred inside a Carbolite Gero EHA 12/300 furnace equipped with a quartz tube for the thermal treatment in a controlled atmosphere. The tube was sealed and connected to the argon cylinder with a gas regulator, which created a constant argon flow (10 L/h). The assembled tube was heated to the target temperature (800 °C for *p*-Br-substituted nickel thiolate or 500 °C for other nickel thiolates) using a two-step temperature program (room temperature to 200 °C, 20 °C/min, and 200 °C to the target temperature, 5 °C/min). The tube was kept at the reaction temperature for 1 h and then allowed to cool to room temperature. The resulting solid material was further analyzed without additional treatment. For the preparation of a sufficient amount of product for further studies and more accurate determination of mass loss values, the thiolate loading was increased to 70-80 mg.

Thermal Decomposition of  $[Ni(S-p-ClC_6H_4)_2]_n$  in an Air Flow at Different Temperatures. Twenty milligrams of  $[Ni(S-p-ClC_6H_4)_2]_n$  was placed in a quartz boat and transferred inside a Carbolite Gero EHA 12/300 furnace equipped with a quartz tube for the thermal treatment in a controlled atmosphere. The tube was sealed and connected to the air compressor, which created a constant air flow (200 L/h). The assembled tube was heated to the target temperature (600, 700, or 800 °C) using a two-step temperature program (room temperature to 200 °C, 20 °C/min, and 200 °C to the target temperature, 5 °C/min). The tube was kept at the reaction temperature for 2 h and then allowed to cool to room temperature. The resulting solid material was further analyzed without additional treatment. For the preparation of a sufficient amount of the product for further studies and more accurate determination of mass loss values, the thiolate loading was increased to 70–80 mg.

Thermal Decomposition of Nickel Thiolates in an Air Flow. Twenty milligrams of nickel thiolate was placed in a quartz boat and transferred inside a Carbolite Gero EHA 12/300 furnace equipped with a quartz tube for the thermal treatment in a controlled atmosphere. The tube was sealed and connected to the air compressor, which created a constant air flow (200 L/h). The assembled tube was heated to 800 °C using a two-step temperature program (room temperature to 200 °C, 20 °C/min, and 200 to 800 °C, 5 °C/min). The tube was kept at the reaction temperature for 2 h and then allowed to cool to room temperature. The resulting solid material was further analyzed without additional treatment. For the preparation of a sufficient amount of product for further studies and more accurate determination of mass loss values, the thiolate loading was increased to 70–80 mg.

#### ASSOCIATED CONTENT

#### **1** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01352.

Additional scanning electron microscopy data for nickel thiolates and products of their thermal decomposition, EDX and XPS spectra of the products of the thermal decomposition of nickel thiolates, powder X-ray diffraction patterns of the nickel thiolates synthesized in different solvents, and GS-MS data for the organic residue after the decomposition of nickel thiolates in an inert atmosphere (PDF)

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# Notes

The authors declare no competing financial interest.

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