

A General Solution-Phase Approach to Oriented Nanostructured Films of Metal Chalcogenides on Metal Foils: The Case of Nickel Sulfide

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Much effort has been made to develop novel methods to prepare nanostructured metal chalcogenides because of their great significance for addressing some basic issues of the quantum confinement effect.¹ However, most of the metal chalcogenides were in the powder form. The oriented growth of one-dimensional (1D) nanomaterials on substrates is considered to be a definitive step toward the fabrication of advanced electronic and optoelectronic nanodevices.² Until now, it still lacks of a general method to fabricate oriented nanostructured films of metal chalcogenides on substrates.

In this communication, we choose nickel sulfide as the example to demonstrate a general solution-phase approach to grow oriented metal chalcogenides nanostructures on the corresponding metal surfaces. Nickel sulfide exhibits interesting compositional, structural, and magnetic properties. It can be used as a hydrodesulfurization catalyst and a cathode in rechargeable lithium batteries.³ Recently, powders of nanostructured nickel sulfide including layer-rolled structure,^{4a} nanorods,^{4b} submicrometer hollow spheres,^{4c} nanosheets, and nanoneedles^{4d} were prepared. Yu and Yoshimura studied the reactions between nickel substrate and sulfur dissolved in different organic solvents at low temperatures and found that Ni₃S₂ thin films, NiS nanowhiskers, and NiS₂ single crystals could be synthesized directly in ethylenediamine.⁵ Here we report for the first time that oriented nanostructured nickel sulfide films ranging from hierarchical dendrites to nanobelts and nanorods can be grown on nickel foils through one-step hydrothermal treatment of sulfur powder and nickel foil.

In a typical procedure, a piece of Ni foil (Aldrich, purity: 99.99%; thickness: 0.127 mm; 1.5 cm × 0.5 cm) and 1 mmol of sulfur powder (Panreac, >99.0% purity) were placed in a 20-mL Teflon-lined autoclave, and then 15 mL of deionized (DI) water (or 15 mL of 6.6 v/v% aqueous hydrazine solution) was added. The autoclave was heated at 180 °C for 12 h and then air cooled to room temperature. The nickel foil was taken out of solution, washed with ethanol, and finally air-dried for characterization. In some cases, an appropriate amount of a surfactant CTAB, cetyltrimethylammonium bromide (Sigma, >99.0% purity), was added into the reaction system.

The morphology, structures, and compositions of the films were investigated by a scanning electron microscope (SEM, LEO 1450VP with an energy-dispersive X-ray instrument). Figure 1 shows the SEM images of different nanostructures of nickel sulfide. Hierarchical dendritic nanostructure of nickel sulfide (Figure 1a) can be grown on the Ni substrate when Ni and S are hydrothermally treated in DI water. The individual dendrites are three-dimensional structures with two long side branches and one short top branch. The side branches possess a shape identical to those of the mother dendrites, while the short top branches, vertically grown on the

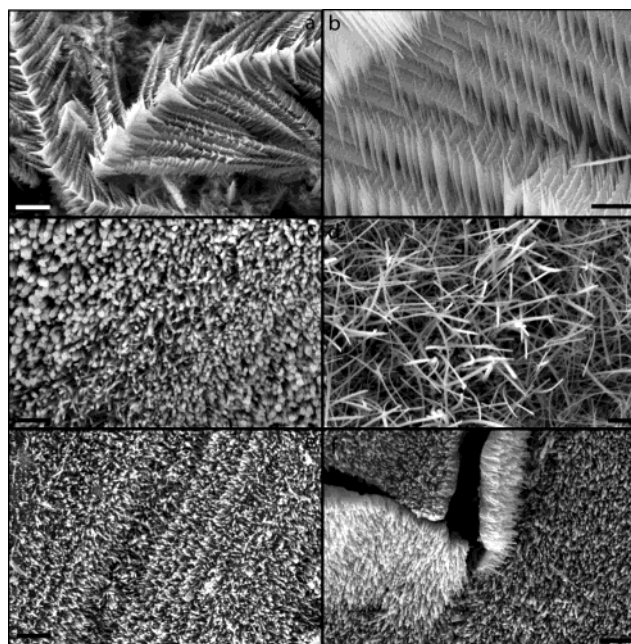


Figure 1. Nanostructured nickel sulfide grown on Ni foils under different conditions: (a) 1 mmol S in DI water; (b) 2 mmol S in DI water; (c) 1 mmol S in aqueous hydrazine solution; (d) 1 mmol S and 0.55 mmol CTAB in aqueous hydrazine solution; (e, f) 1 mmol S and 2.2 mmol CTAB in aqueous hydrazine solution. Scale bar: 2 μ m.

trunk, have three identical secondary branches. When the amount of S increases from 1 mmol to 2 mmol, the branches of the dendrites possess nearly parallel secondary branches with two sharp nanotips (Figure 1b). If aqueous hydrazine solution is used as the reaction media instead of DI water, vertically aligned nanorod arrays can be obtained (Figure 1c). The nanorods have nonuniform diameters over the range of 50–500 nm.

It was found that the shape and size of nickel sulfide nanostructures grown in the aqueous hydrazine solution could be controlled by the amount of CTAB added. Nanobelts were formed with the addition of 0.55 mmol CTAB, while smaller-sized nanorods were obtained when 2.2 mmol of the surfactant was used. The nanobelts were 50–400 nm in width and several to tens of micrometers in length. The rectangle-like cross section of the materials is clearly observed in Figure 1d. Their width-to-thickness ratios are about 2 to 4, and the thickness is less than 80 nm. Figure 1e shows the nickel sulfide nanorod arrays grown on Ni surface in the presence of CTAB. These nanorods are relatively uniform and have diameters less than 60 nm, significantly smaller than that synthesized in the absence of CTAB. Their lengths are in the range of 0.5–2 μ m, as observed from Figure 1f. Energy-dispersive X-ray (EDX) analysis shows only Ni and S. The absence of bromide, nitrogen, and carbon in the resulting product indicates complete removal of the surfactant.

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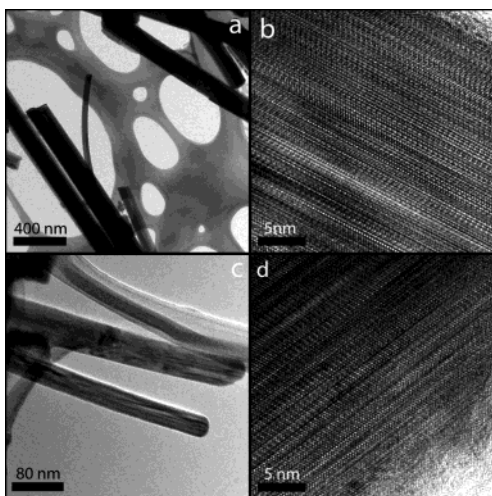


Figure 2. TEM and HRTEM images of nickel sulfide nanobelts (a, b) and nanorods (c, d) synthesized in the presence of CTAB.

The X-ray diffraction patterns (Supporting Information) of the resulting nickel sulfide films reveal a rhombohedral phase [space group: $R\bar{3}2(155)$] of Ni_3S_2 (Heazlewoodite, JCPDS file No. 44-1418) with calculated lattice contents $a = 5.745(4)$ Å and $c = 7.135(0)$ Å. The films prepared in the presence of CTAB show an additional rhombohedral phase of NiS (Millerite, space group: $R3m(160)$, JCPDS file No. 86-2280) with calculated lattice contents $a = 9.620(0)$ Å and $c = 3.149(0)$ Å.

The microstructures of nickel sulfide nanobelts and nanorods synthesized in the presence of CTAB were further examined by transmission electron microscopy (TEM, Tecnai 20, FEG) images (Figure 2). Figure 2a confirms the belt-like structure of the nickel sulfide nanobelts. A representative high-resolution transmission electron microscopy (HRTEM) image of an individual nanobelt (Figure 2b) shows that the nickel sulfide nanobelts have stacking faults. Panels c and d of Figure 2 show the TEM and HRTEM images of the nickel sulfide nanorods. The nanorods are also found to be single crystals with stacking faults. These stacking faults make it difficult to analyze the images any further.

To study the effect of substrate geometry on the formation of 1D nanomaterials, we substituted the Ni foil with fine Ni powders. Interestingly, only spherical particles of nickel sulfide were obtained. This must be due to the omnidirectional release of Ni^{2+} from Ni powders during hydrothermal treatment. The geometry of a foil obviously favors a more or less unidirectional diffusion of metal ions resulting in the observed vertical growth. We also found that hydrazine was required in growing 1D nanomaterials on a metal surface. Without hydrazine, 1D nickel sulfide could not be obtained even in the presence of CTAB. It was reported that hydrazine could be used as the solvent for the synthesis of zinc telluride nanorods through forming a complex between hydrazine and zinc ions.^{6b} In our study, hydrazine is believed to assist the dissolution and reduction of sulfur and coordinate the nickel ions by forming the complex $[\text{Ni}(\text{N}_2\text{H}_4)_3]^{2+}$.⁶ In the absence of hydrazine, the slower dissolution of sulfur powder in DI water under hydrothermal treatment could not provide a sufficient amount of S^{2-} . This nonequilibrium growth would produce hierarchical dendrites of nickel sulfide through oriented aggregation,⁷ while the coordination between hydrazine and nickel ions is thought to be the reason for the formation of 1D nickel sulfide.

A series of oriented nanostructured metal chalcogenides films have been fabricated by hydrothermal treatment of the corresponding metal foils and chalcogen elements (Supporting Information), indicating the generality of this approach. These materials are exciting additions to a newly emerging family of oriented nanowires, nanorods, and nanotubes.⁸ The chalcogenides may also be grown on other hydrothermally stable substrates such as silicon wafer precoated with a metallic layer.

The physical and chemical properties of nanostructures depend on their architectures, including geometry, morphology, and hierarchical structures.⁹ The tunable nanostructured nickel sulfide films on Ni foils provide new building blocks for nanodevices. They should also be ideal candidates for studying the nanoarchitecture-dependent performance as cathodes in micro-rechargeable lithium batteries.

Supporting Information Available: XRD patterns, EDX spectrum of nanostructured nickel sulfide, and SEM images of NiS synthesized under other conditions and additional metal chalcogenides. The material is available free of charge via the Internet at <http://pubs.acs.org>.

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