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Is NiCo₂S₄ really a semiconductor?

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ABSTRACT: NiCo₂S₄ is a technologically important electrode material that has recently achieved remarkable performance in pseudocapacitor, catalysis, and dye-synthesized solar cell applications.¹⁻⁵ Essentially, all reports on this material have presumed it to be semiconducting, like many of the chalcogenides, with a reported band-gap in the range of 1.2-1.7 eV.^{6,7} In this report, we have conducted detailed experimental and theoretical studies, most of which done for the first time, which overwhelmingly show that NiCo₂S₄ is in fact a metal. We have also calculated the Raman spectrum of this material and experimentally verified it for the first time, hence clarifying inconsistent Raman spectra reports. Some of the key results that support our conclusions include: (1) the measured carrier density in NiCo₂S₄ is $3.18 \times 10^{22} \text{ cm}^{-3}$, (2) NiCo₂S₄ has a room temperature resistivity of around $10^3 \mu\Omega \text{ cm}$ which increases with temperature, (3) NiCo₂S₄ exhibits a quadratic dependence of the magnetoresistance on magnetic field, (4) thermopower measurements show an extremely low Seebeck coefficient of $5 \mu\text{V K}^{-1}$, (5) first principles calculations confirm that NiCo₂S₄ is a metal. These results suggest that it is time to re-think the presumed semiconducting nature of this promising material. They also suggest that the metallic conductivity is another reason (besides the known significant redox activity) behind the excellent performance reported for this material.

NiCo₂S₄ has a normal thiospinel crystal structure⁸ and was first described in 1850 upon discovery in the Stahlberg Mine in Müsen, Siegerland, North Rhine Westphalia, Germany, and was named for that locality. Previous report shows that siegenite could deliver a high conductivity of $1.25 \times 10^6 \text{ s m}^{-1}$ at room temperature.⁹ The siegenite (NiCo₂S₄) system has recently become a heavily studied electrode material for energy applications, including dye-sensitized solar cells (DSSCs), supercapacitors, and fuel cells with excellent results. For instance, Banerjee *et al.* reported that NiCo₂S₄ based DSSCs show a high catalytic activity towards the I⁻/I³⁻ redox couple, and lead to an impressive efficiency of 6.9%, compared with 7.7% obtained with a Pt electrode in similarly constructed devices.¹⁰ This replacement of Pt by NiCo₂S₄ enables a low-cost DSSC device since the Pt catalyst accounts for nearly 50% of the cost.³ Further, it has been demonstrated by many groups that nanostructured NiCo₂S₄ can be used in fuel cells and supercapacitors with very good energy conversation and storage performance.^{3, 7, 11-13} These good device performances across many applications have commonly been attributed to the high conductivity of NiCo₂S₄, which has recently been attributed to its narrow band gap, implying that NiCo₂S₄ is a typical semiconductor. While the thiospinel siegenite has been widely studied for energy harvesting and storage applications, its fundamental properties have actually remained poorly studied. Even its Raman spectrum remains unknown.

Here we show that the sporadic reports on its physical properties have not firmly established the correct properties of this material. For example, Chen *et al.* re-

ported that siegenite is a semiconductor with a direct band gap of 1.2 eV using UV-Vis measurements.⁶ Du *et al.* concluded that siegenite was semiconducting with a direct transition of 1.71 eV.⁷ Furthermore, Yang *et al.* showed that the F_{2g} and A_{1g} Raman modes of NiCo₂S₄ are located at 523.5 and 671.2 cm⁻¹, respectively.¹⁴ Unfortunately, as demonstrated later in the manuscript, all the above-mentioned reports on the basic properties of NiCo₂S₄ are inaccurate. Hence, we felt that more detailed studies are needed to understand the origin of the remarkably good performance of this material in various applications.

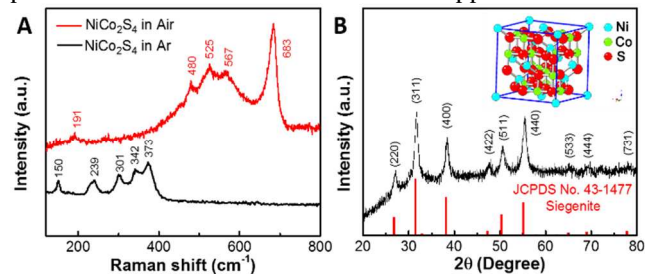


Figure 1. (A) Typical XRD pattern of as-prepared NiCo₂S₄ at room temperature, with the crystal model as inset. (B) Raman spectrum measured in air and argon atmosphere.

As a typical normal spinel, the crystal structure of (Ni)_A[(Co)₂]_BS₄ was verified by neutron diffraction by Nakagawa *et al.*⁸ Nickel and Cobalt are found to occupy tetrahedral sites (A) and octahedral sites (B), respectively. In a unit cell, only one eighth of the A sites are occupied by Ni²⁺ and half of the B sites are occupied by Co³⁺. The inset

of Figure 1a represents the crystal structure of NiCo_2S_4 with space group $F\bar{d}3m$. The XRD patterns of as-synthesized NiCo_2S_4 are shown in Figure 1a. All diffraction peaks can be recognized as the standard NiCo_2S_4 thiospinel structure with no detectable secondary phases. The lattice constant of NiCo_2S_4 was calculated to be 9.319 Å according to the strongest diffraction peak (311), consistent with previous investigations.³ Notably, the full width at half maximum (FWHM) of the peaks for the as-obtained thiospinel was broad, clearly illustrating that the samples were nanocrystalline in nature. The average grain size of the nanocrystal was estimated to be 10.32 nm based on the FWHM (0.8°) of the strongest peak (311) and the empirical Scherrer formula $d = 0.9\lambda/(\beta\cos\theta)$, in which β and θ are the FWHM (in radian) and Bragg angle, respectively. Although the diffraction intensity of all peaks was somewhat low, the relative intensity among the diffraction peaks was consistent with the standard nickel cobalt thiospinel structure, indicative of the successful and controlled synthesis of NiCo_2S_4 by the hydrothermal method.

Table 1: Experimental and calculated Raman Vibration mode of NiCo_2S_4

	A_{1g}	E_g	$T_{2g,1}$	$T_{2g,2}$	$T_{2g,3}$
Experiment	373	239	342	301	150
Calculation	401	253	364	322	163
Difference	-6.9%	-5.5%	-6.0%	-6.5%	-7.9%
Atoms involved	S	S	S, Ni	S, Ni	S, Ni

The lattice dynamics of NiCo_2S_4 has never been well-studied except for one literature report showing Raman active T_{2g} (523.5 cm^{-1}) and A_{1g} (671.2 cm^{-1}) modes under atmosphere.¹⁴ However, those vibration modes are much closer to the features of typical spinel oxides (NiCo_2O_4).¹⁵ In addition, there is apparently no calculation of the Raman modes of NiCo_2S_4 . Given that the sulfides are easily oxidized by laser heating during measurement,¹⁶ Raman scattering experiments should be performed carefully to exclude the unintentional oxidation of the NiCo_2S_4 phase. Therefore, we employed Argon atmosphere to measure the Raman features of NiCo_2S_4 . The results are shown in Fig. 1b. For comparison, the Raman spectra measured in air are also shown in Figure 1b. Actually, all observed modes for the sample measured in air can be indexed as Raman features of NiCo_2O_4 .¹⁷ A third Raman measurement was done, where the data was collected in air while inserting a filter between the sample and laser (Figure S1). The data in Figure S1 show a superposition of two sets of Raman vibration modes from NiCo_2S_4 and NiCo_2O_4 , clearly indicating that laser induced oxidation takes place. A similar phenomenon was also observed in the Fe_3S_4 system.¹⁶ In order to check the validity of the experimental Raman results for NiCo_2S_4 , a theoretical analysis based on the normal thiospinel NiCo_2S_4 was performed. This analysis predicts five Raman active modes: E_g , A_{1g} and three T_{2g} . The calculated and experimental frequencies of the Ra-

man active modes are summarized in Table 1. The stretching of S atoms towards the tetrahedral site Ni atom and the bending of the S- Ni_{tetra} -S bonds causes the A_{1g} (373 cm^{-1}) and E_g (239 cm^{-1}) mode, respectively. The three T_{2g} modes (150 , 301 , and 342 cm^{-1}) can be ascribed to asymmetric bending of S- Ni_{tetra} -S bonds. All the calculated frequencies agree well with the experimental values with less than 10% difference.

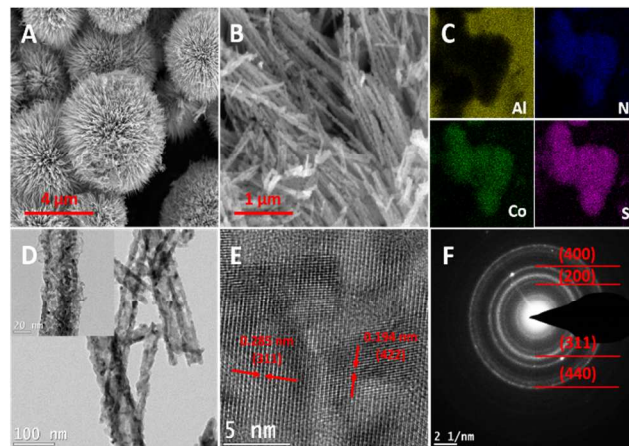


Figure 2. (A-C) Representative FESEM images of as-prepared NiCo_2S_4 with corresponding EDX element mapping of aluminum, nickel, cobalt and sulfur. (D-F) Typical TEM and HRTEM images of the nanostructured samples with corresponding SAED pattern.

Figure 2a-b show that the hydrothermally obtained powders of NiCo_2S_4 maintain a uniform urchin-like morphology with nanocrystalline self-assembled nanotube emanating radially grown from the center. These hollow nanotubes likely result from the well-known Kirkendall effect of the sacrificial precursor template during the anion ion exchange process.¹⁸ Energy dispersive spectra (EDS) were collected to provide further insight into the elemental composition and distribution of the as-prepared NiCo_2S_4 . An even distribution of the elements Ni, Co, and S (Figure 2c) on the surface is clearly visible, further demonstrating the successful preparation of high quality thiospinel NiCo_2S_4 . The corresponding signal of Al is from the sample holder. Figure 2d-f shows the TEM images of the NiCo_2S_4 nanotube and corresponding selected area electron diffraction (SAED). The representative TEM image shows the NiCo_2S_4 nanotubes with a diameter of about 50 nm, with the individual nanotube itself composed of numerous nanocrystallites of around 10 nm size, consistent with the results from the SEM and XRD analyses. The high resolution TEM image reveals that the lattice plane distances are 0.285 and 0.194 nm, which fits well to the (311) and (422) interplanar spaces in siegenite. The lattice fringes with different orientations suggest that the as-obtained NiCo_2S_4 is polycrystalline in nature, which is confirmed by its corresponding SAED. The supercapacitor performance of as-prepared NiCo_2S_4 nanopowder was checked and is shown in Figure S2.

It has been reported that thiospinel NiCo_2S_4 has a much higher conductivity than its oxide counterpart (NiCo_2O_4) and that it is a semiconductor with a direct band gap of 1.2 eV based on UV-Vis measurements.⁶ Yet, the reported UV-Vis spectra^{6,19} showed a nearly straight line, unlike the UV-Vis spectra of typical semiconductors,²⁰ implying that no absorption has actually occurred during the measurement. We observe a similar behavior in our material and find it hard to make any definite conclusion from UV-Vis measurements (Figure S3). Therefore, we have studied the transport behavior using pellets prepared by pressing NiCo_2S_4 powder, as shown in Figure 3a. We were surprised to observe that NiCo_2S_4 actually conducts like a typical metal with a positive temperature coefficient of resistance. Notably, the resistivity of NiCo_2S_4 increased linearly in the temperature range of 40 to 300 K. The linear relationship between resistivity and temperature ($\rho_{xx} \propto T$) confirms its metallic behavior and shows that electron-phonon scattering dominates in NiCo_2S_4 . The room temperature resistivity of our NiCo_2S_4 sample is approximately $10^3 \mu\Omega \text{ cm}$, indicating excellent conductivity. The Seebeck coefficient of pressed NiCo_2S_4 pellets was measured as a function of temperature and the results are shown in Figure S4. An extremely low value of around $5 \mu\text{V K}^{-1}$ was obtained, which strongly supports the metallic nature of thiospinel NiCo_2S_4 . Further, an illustration of the good conductivity, in comparison to other known semiconducting materials, is shown in Figure S5. It can be seen that the conductivity of as-prepared NiCo_2S_4 is much higher than the typical semiconductors such as Co_3O_4 and NiCo_2O_4 .

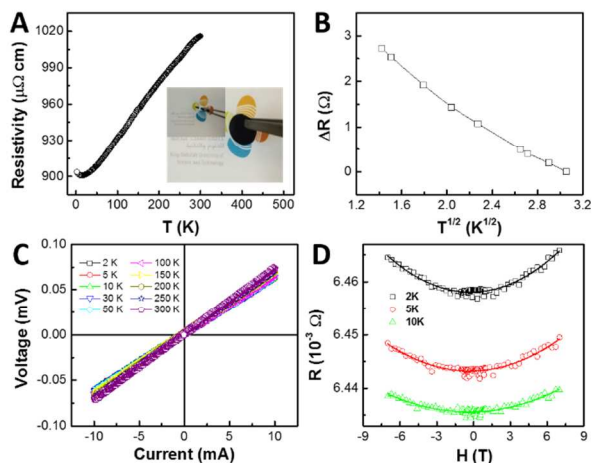


Figure 3. (A) Resistivity of NiCo_2S_4 as a function of temperature. (B) ΔR versus $T^{1/2}$ at low temperature and (C) Voltage-current (I-V) curves and (D) magnetoresistance against magnetic field for various temperatures. Note that the inset of (A) shows a photo of the pressed NiCo_2S_4 pellet.

Attributed to the severe interfacial scattering among the nanoparticles, the residual resistivity at 2 K is rather large with $\rho_{2\text{K}}/\rho_{300\text{K}} \approx 0.9$, meaning that much higher conductivity can be expected in NiCo_2S_4 single crystals or epitaxial thin films. Interestingly, the resistivity increases slightly for $T < 20$ K with decreasing temperature, which can be ascribed to the quantum three-dimensional weak

localization effect. According to this effect, a linear dependence of ΔR on \sqrt{T} is expected and observed (Figure 3b). It is believed that the weak localization is caused by the electron scattering from defects and interfaces between the crystal grains.²¹ In order to check the data accuracy, voltage-current (IV) curves were measured in a four-terminal setup at different temperatures, as shown in Figure 3c. Obviously, all the acquired IV curves are linear in the range of -10 mA to 10 mA indicating an Ohmic behavior. Figure 3d displays the magnetoresistance of NiCo_2S_4 as a function of the magnetic field at low temperatures. A pronounced positive and quadratic behavior is observed, which is one of the characteristics of normal metals. The magnetoresistance measurement verified the metallic nature of NiCo_2S_4 . A slight discrepancy of the magnetoresistance at $H = \pm 7$ T originates from a weak interference of the Hall signal due to minor geometric misalignment. Breakdown of the weak localization at low temperature is usually expected under magnetic field, indicative of a small negative magnetoresistance ($\sim -0.1\%$) at low fields. Yet, this phenomenon is not observed in our case, probably because we approach the sensitivity limit of the equipment.

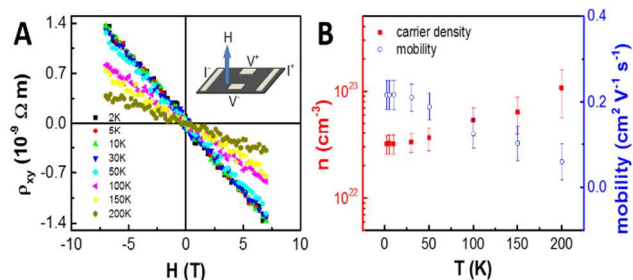


Figure 4. (A) Magnetic field dependent Hall resistivity of NiCo_2S_4 at different temperatures. The inset gives the Hall measurement configuration. (B) Calculated carrier density (red) and mobility (blue) as a function of temperature.

The Hall resistivity of the pressed NiCo_2S_4 pellet is presented in Figure 4a, in which all the curves are corrected by removing the longitudinal resistance contribution. The measurement configuration is given in Figure 4a as an inset. The linear dependence of the Hall resistivity as a function of the magnetic field in the whole temperature range, with a negative slope, indicates that the electrical transport in NiCo_2S_4 is dominated by electrons instead of holes. The carrier density can be obtained using the slope of the curves ($R_{xy} = R_0 H$, Hall coefficient $R_0 = 1/ne$) in Figure 4a. Moreover, the electron mobility is calculated through $\mu = R_0/\rho_{xx}$. Figure 4b presents the carrier density and electron mobility as a function of temperature. The carrier density and mobility of the NiCo_2S_4 pellet remain nearly constant, with fluctuations on the same order of magnitude as the change in the parameters over the studied temperature range. The carrier density at 2 K is calculated to be $3.18 \times 10^{22} \text{ cm}^{-3}$, which is as high as that of silver ($8.37 \times 10^{22} \text{ cm}^{-3}$). The relatively low mobility is probably related to defect scattering in the nanocrystalline samples.

Furthermore, first principles calculations were carried out to determine if theory can confirm the experimental results showing the metallic nature of this compound. According to neutron diffraction, the crystal structure of NiCo_2S_4 is a normal spinel.⁸ Starting from the experimental structural parameters, we arrive at a lattice constant of 9.274 Å after structure optimization, which is in good agreement with the measured value of 9.319 Å. Our calculations show non-spin polarization. According to the densities of states shown in Figure 5, there is strong hybridization between the S p states, and the Ni and Co d states near the Fermi level (0 eV). Electronic bands are crossing the Fermi level, which is reflected by a finite density of states. Hence, NiCo_2S_4 is undoubtedly metallic, and the theoretical calculation is in accord with our experimental results.

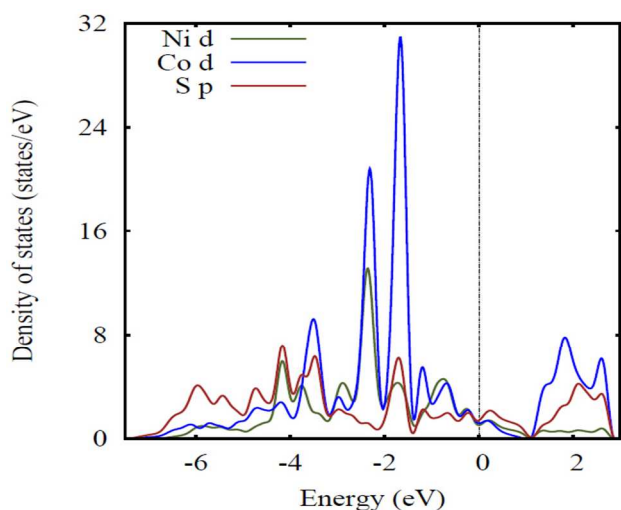


Figure 5. Site projected density of states of NiCo_2S_4 .

In summary, single phase powders and pellets of thiospinel NiCo_2S_4 were successfully synthesized by the hydrothermal method. Several experimental and theoretical analyses reveal that NiCo_2S_4 is in fact a metal rather than a semiconductor, in contrast to has been recently reported. This conclusion explains the excellent electrochemical performance reported for this compound in a wide spectrum of applications (supercapacitors, fuel cells, and solar cells). We believe that in addition to good electrochemical activity of the cations (Ni and Co), the metallic conductivity of NiCo_2S_4 is a key factor in the excellent performance it has achieved in various applications.

ASSOCIATED CONTENT

Supporting Information. Experimental details, Raman measurement, supercapacitor performance, Seebeck coefficient and the illustration of conductivity of NiCo_2S_4 are included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

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