

Studying the Effect of Absorption of Organic Molecules on Rare Earth Chalcogenide Aerogels NaRESnS₄ (RE= Y, Gd, or Tb) at Room temperature using Uv-Vis and FTIR

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ABSTRACT: *In this paper, we have explored the ability of the rare earth chalcogels, NaRESnS₄ (RE= Y, Gd, or Tb) to discriminate among different organic molecules, e.g., Tetracyanoethylene (TCNE), Anthracene and Tetrathiafulvalene (TTF), by their electronic structures. We have noticed blending rare earth chalcogels with TCNE (electron acceptor molecules) at room temperature causes a noticeable shift in the band gap; approving these chalcogels to be candidates for some applications such as optical devices and sensors.*

KEYWORDS -Chalcogel; Mesoporous; Organic molecules; Separation

I. INTRODUCTION

Recently, the possibility of the synthesis and characterization of a new class of the metal chalcogenide aerogels have been investigated by Edhaim, Fatimah and Rothenberger, Alexander.^[1] We have noticed that chalcogels are typically synthesized using various chalcogenide building blocks and transition metal linkers. Therefore, we have proved that the chalcogels is not limited to the transition metals; instead, it can be constructed from the rare earth metal ions, e.g., Y, Gd or Tb, Fig. 1. We have also explored the effect of the presence of these metals on the adsorption properties of the materials. The results revealed that the rare earth chalcogels possessed high BET surface areas and showed preferential adsorption of polarizable gases and hydrocarbons. The adsorption capacity of these chalcogels toward toluene and CO₂ selectivity are much higher than most reported chalcogels, activated carbon, 13x-zeolite and silica gels.^[1]

In this work, however, we explored the ability of the rare earth chalcogels NaRESnS₄ (RE= Y, Gd, or Tb) to discriminate among different organic molecules, e.g., Tetracyanoethylene (TCNE), Anthracene and Tetrathiafulvalene (TTF), by their electronic structures. This application has not been investigated for the rare earth metal chalcogenide aerogels. The results confirmed that these aerogels tend to absorb electron-acceptor molecules affecting the FTIR bandgap and UV spectra. Hence, Rare Earth aerogels could be used as

sensors. The absorbed amount has been calculated using beer-lambert law.

II. EXPERIMENTAL

2.1 Absorption of Organic Molecules

Inside a glovebox, around 50 mg of each chalcogels was soaked in a 10 mL of anhydrous chloroform containing tetrathiafulvalene (TTF; 16 mg, 0.08 mmol), anthracene (14 mg, 0.08 mmol), or tetracyanoethylene (TCNE; 10 mg, 0.08 mmol) at room temperature for 48 hours. The products were isolated by filtration, washed several times with anhydrous chloroform, and dried in a vacuum oven at room temperature for 24 hours. Finally, the products were ground into powder for infrared and UV-Vis spectroscopy measurements. To confirm the absorption of organic molecules, FTIR spectroscopy was carried out on a Nicolet 6700 FTIR spectrometer in the mid-IR region (500-4000 cm⁻¹) with a resolution of 2 cm⁻¹. UV-Vis spectra of the TCNE/chloroform solution were recorded before and after the treatment with the chalcogels in the 200-800 nm regions to estimate the absorbed amount of organic compound. Different concentration of TCNE/chloroform solutions (0.1x10⁻⁴M, 0.3x10⁻⁴ M, 0.5x10⁻⁴ M) was used to determine the maximum wavelength (λ_{max}) at the highest absorbance intensity (A). Beer-Lambert's law then was applied to quantify the amount absorbed by the chalcogels and determines the residual concentration of the TCNE solution.

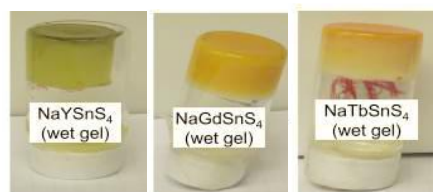


Figure 1 Visual representation of the rare earth chalcogels before drying processes.

III. RESULTS AND DISCUSSION

The high surface area with accessible pores of the resulting chalcogels comparing to the carbon and metal oxide materials allow the surface interaction with guest molecules. Therefore, the ability of the chalcogels to differentiate between different organic molecules from their electron structures was investigated. The materials were soaked in chloroform solutions containing electron-donor tetrathiafulvalene (TTF) molecules, electron-acceptor tetracyanoethylene (TCNE) molecules, and inert anthracene molecules for around 48 hours.^[2] FTIR spectroscopy proves the presence of TCNE molecules within chalcogel structures, Fig. 2.

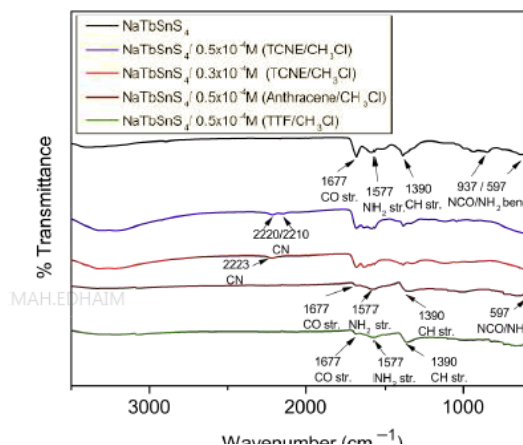
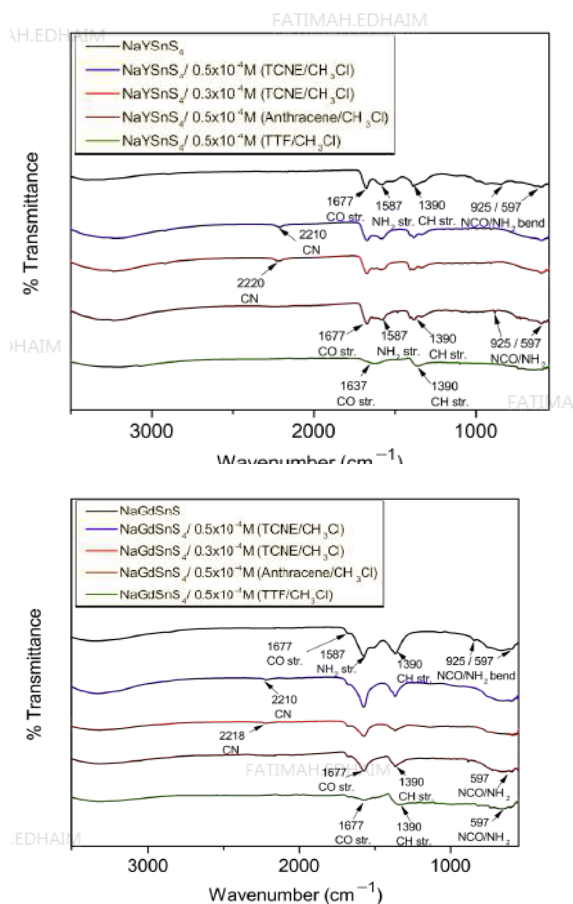


Figure 2 FTIR spectra of the rare earth chalcogels before and after the treatment with organic molecules

The sharp infrared absorption peaks of 2214, 2260, 2227 cm^{-1} are the characteristic vibration modes of free TCNE that rise from the nitrile groups ($\text{C}\equiv\text{N}$).^[3] Resulting chalcogels as synthesized do not show any absorption peak bands in this area. However, after the treatment with TCNE molecules, some vibration peaks appear at 2225, and 2210 cm^{-1} confirming the incorporation of the TCNE molecules into the chalcogels. These values are consistent with the reported $\text{Ln}(\text{TCNE})_3$ ($\text{Ln} = \text{Dy}, \text{Gd}$).^[3] The slight shift of these peaks to lower frequencies meet the bands of common TCNE incorporate electron donor complexes.^[4]

It is expected the low-lying π^* orbitals in the $\text{C}\equiv\text{N}$ group grab electron density from the chalcogel networks. Remaining FTIR peaks in the 597 ($\nu\text{NCO}/\text{NH}_2$), 1390, 2854 ($\nu\text{C}-\text{H}$) 1677 ($\nu\text{C}=\text{O}$), and 1577, 3418 (νNH_2) cm^{-1} region belong to the residual formamide ligand in the chalcogel frameworks.^[5]

The changes of the electronic structure and the properties of the chalcogels after the treatment with TCNE were proved by UV-Vis spectra of chalcogels. Different concentrations of TCNE were prepared and measured by UV-Vis spectroscopy to confirm the charge transfer. TCNE has a band gap in the region of 4.03.8eV to 4.10eV.

The UV-Vis spectra after the treatments with TCNE show a remarkable blue shift for the chalcogel energy gaps. The band gap is 3.14eV for $\text{NaYSnS}_4/\text{TCNE}$ ($0.5 \times 10^{-4} \text{ M}$), 3.28eV for $\text{NaYSnS}_4/\text{TCNE}$ ($0.3 \times 10^{-4} \text{ M}$), 3.49eV for $\text{NaGdSnS}_4/\text{TCNE}$ ($0.5 \times 10^{-4} \text{ M}$), 3.63eV for $\text{NaGdSnS}_4/\text{TCNE}$ ($0.3 \times 10^{-4} \text{ M}$), 3.12eV for

NaTbSnS₄/TCNE (0.5x10⁻⁴ M) and 3.94eV for NaTbSnS₄/TCNE (0.3x10⁻⁴ M), Fig. 3.

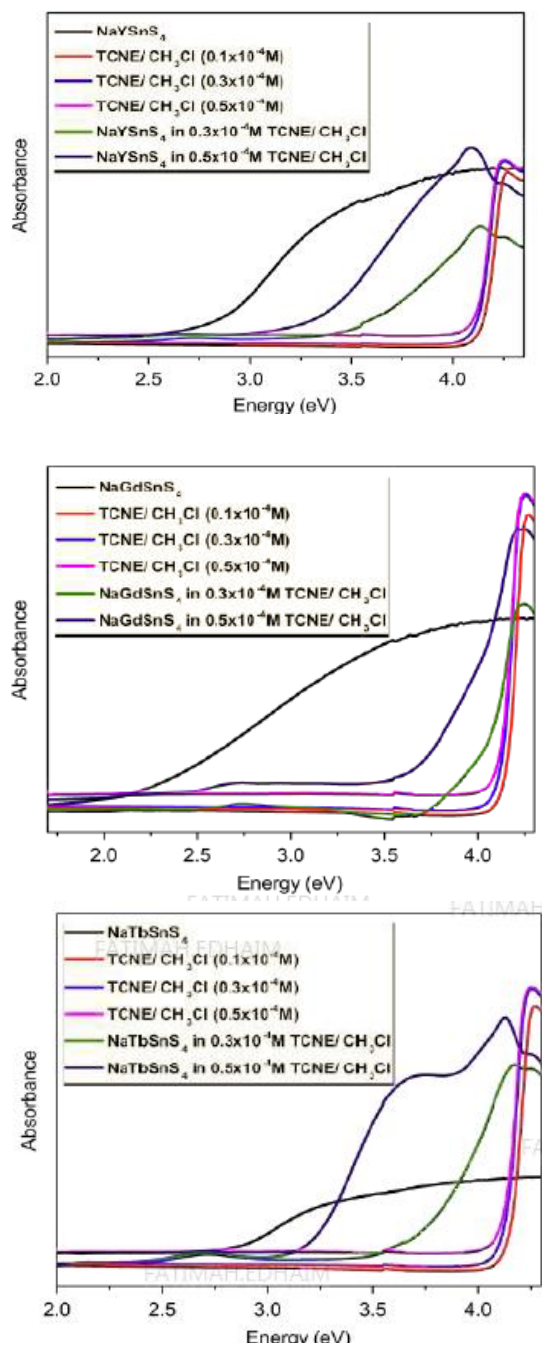


Figure 3 UV-Vis spectra of the rare earth chalcogenides before and after the treatment with different concentration of TCNE/ CH₃Cl confirming the incorporation of the TCNE and showing the blue shift of the chalcogel band gaps.

This observation indicates that the merger of electron acceptor molecules such as TCNE molecules into RE-chalcogel networks leads to

charge transfer interaction where the chalcogel serves as an electron donor. The lowest unoccupied molecular orbital (LUMO) of TCNE combined with the rare earth chalcogels conduction band, resulting in increasing of the conduction band energy and a blue shift of the UV-Vis spectra. The blue shift in the rare earth chalcogel band gaps after TCNE absorption implies the change in the electronic density of the chalcogels caused by stronger interaction between TCNE molecules and the resulting chalcogels comparing to the redshift of the reported chalcogels.^[1, 6] The UV-Vis absorbance intensity of known concentration of TCNE/CHCl₃ solutions (0.1x10⁻⁴ M, 0.3x10⁻⁴ M and 0.5x10⁻⁴ M) and supernatant TCNE/ CHCl₃ solution after the treatment with chalcogels were used to calculate the adsorbed amount of TCNE, Fig. 4.

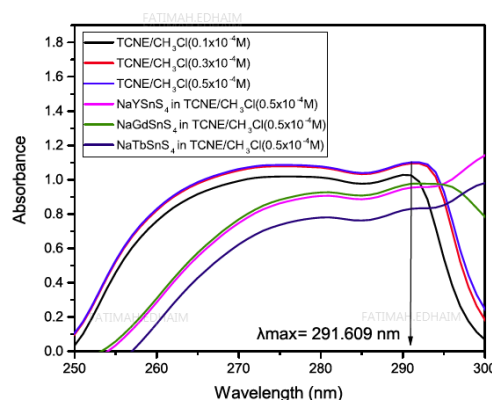


Figure 4 UV-Vis spectra of the supernatant solutions of different concentration of TCNE in CH₃Cl before and after the treatment with chalcogels showing the maximum wavelength of TCNE.

To calculate the adsorbed amount of TCNE, Lambert-Beer law was used. From the UV-Vis spectrum, TCNE/CH₃Cl (0.5 x 10⁻⁴ M) has a maximum absorption (A (λ_{max})) of 1.10469 at 291.609 nm. So, the calculated molar absorption coefficient (ε) of TCNE in CH₃Cl solution at 291.609nm = 22093.8 M⁻¹cm⁻¹, which is close to the average absorption of TCNE in various solvents.^[7] The calculated residual concentration of TCNE in CH₃Cl solution after the treatment with chalcogels was 0.431 x 10⁻⁴ M for NaYSnS₄, 0.438 x 10⁻⁴ M for NaGdSnS₄, and 0.377 x 10⁻⁴ M for NaTbSnS₄.

Noteworthy, incorporation of FTT, which are electron donor molecules and anthracene, which are neither donor nor acceptor molecules, do not affect the electronic structures of chalcogels, Fig. 2. This finding shows that the chalcogels are active toward electron acceptor adsorbates, which means a possible usage of these materials in sensor and thin film transistor applications.

IV. CONCLUSION

Blending rare earth chalcogels with TCNE (electron acceptor molecules) at room temperature causes a noticeable shift in the band gap; approving these chalcogels could be candidates for some applications such as optical devices, thin film transistors, and sensors. The initial results indicate that rare earth chalcogels could be useful materials for purification and separation of hydrocarbon and gas molecules. However, as the polarizability of the chalcogels significantly affects the adsorption and separation processes, improvements of these processes could be achieved using more polarizable alkali metal ions like K or Rb, and building blocks containing Se or Te atoms like A_4SnQ_4 ($A = K$ or Rb , $Q = Se$ or Te).

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