Characterizations of Tungsten Nitride and Sulfide Aerogels Formed using a Modified Sol-Gel Approach

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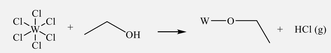
Introduction

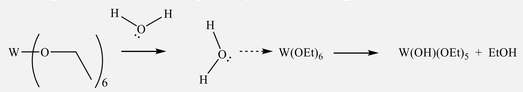
Nanoparticles have become essential to many applications in today's world. Tungsten Nitride is being studied for its conductive properties. Tungsten Sulfide is a catalyst, in hydrodesulfurization and hydro denitrification. The purpose of this experiment is to determine if the addition of structural directing agents, such as urea and thiourea, will alter the morphology and increase the surface area of the aerogel. The aerogel was synthesized using an economically efficient process called the sol-gel epoxide addition method.

Method

The method starts with the formation of a metal alkoxide when ethanol is mixed with tungsten (VI) chloride. A proton of the hydroxyl group on ethanol is reacts with a chloride to produce HCl (g). Tungsten is then attacked by ethoxy groups to make tungsten ethoxide.

(1) 

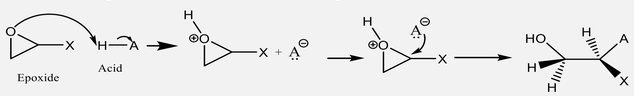
The next step involves the hydrolysis of tungsten ethoxide to

(2) 

form a tungsten metal complex, which undergoes condensation reactions that results in an oxo- or hydroxo- group bridged between two tungsten complexes and water.

(3) $W(OH)(OEt)_5 + W(OH)(OEt)_5 \rightarrow (OEt)_5—W—O—W—(OEt)_5 + H_2O$

Next, the epoxide initiates gelation to create a 3D-structural network. It behaves as a proton scavenger by taking protons from reagents/products (e.g. polyacrylic acid, H_3O^+, and ethanol) in the different reactions taking place. With the proton removed, these compounds behave as nucleophiles.



The sol-solution was aged for 12-14 days for the gel network to form. The gel was soaked in an ethanol bath to replace residual solvent. It was dried in a critical point extractor using supercritical-CO_2 to produce a low density, highly porous, large surface area aerogel. The aerogel was annealed in a tube furnace with a vapor source (e.g. ammonium carbonate or sublimed sulfur) to make tungsten nitride or tungsten sulfide nanoparticles, respectively.

The material was characterized using IR spectroscopy, powder x-ray diffraction (PXRD), and scanning electron microscopy.

Results

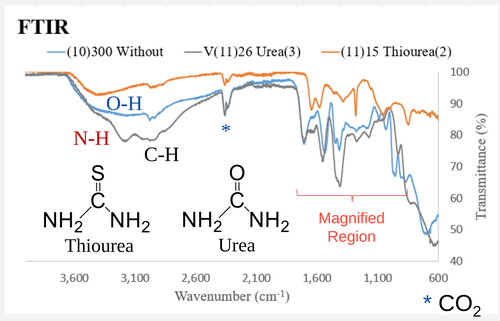
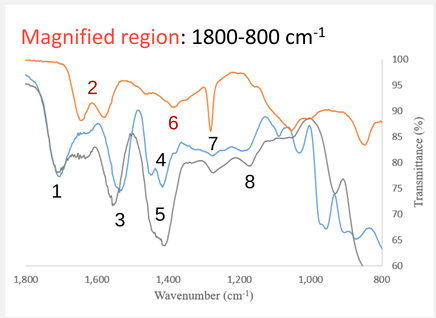
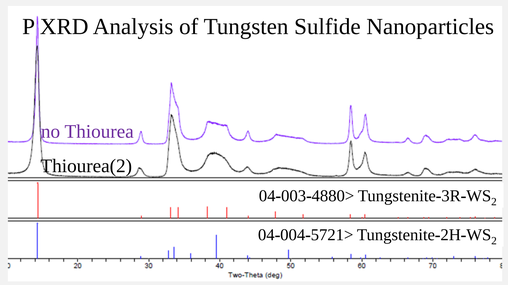


Table 2: IR Interpretation

#	Functional Group
1	C=O (1703 cm^{-1})
2	C=N, NH_2 bend
3	N-O (1550 cm^{-1})
4	O-H (1400 cm^{-1})
5	O-H (1400 cm^{-1})
6	C-H (1375 cm^{-1})
7	C-N (1180 cm^{-1})
8	C-O Stretching





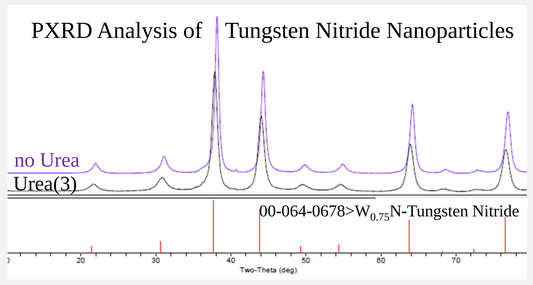
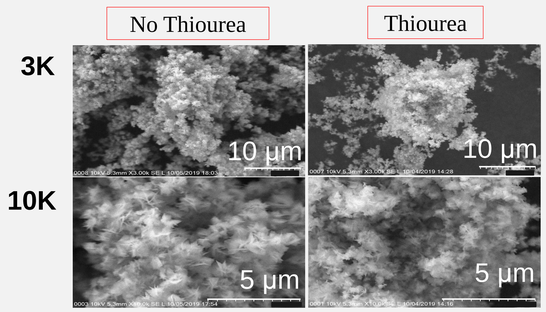


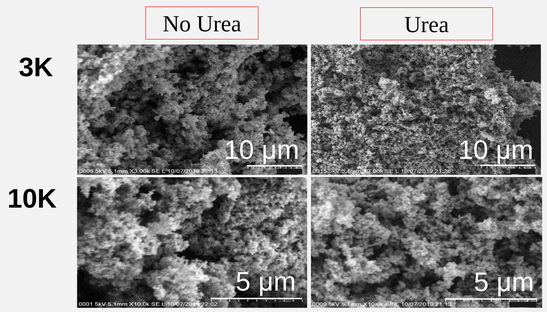
Table 2: Peak Profile Analysis for Particle Size

Material	Diffraction angle by °2θ (particle size in nm)				
WS_2 - No TU	14.3 (1)	33.0 (1)	33.9 (5)	58.3 (2)	60.5 (1)
WS_2 - TU(2)	14.3 (1)	32.7 (1)	33.0 (2)	58.4 (2)	60.4 (2)
$W_{0.75}N$	37.6 (1)	43.7 (1)	63.6 (1)	76.1 (1)	

Annealed 700°C for 8hrs with Sublimed sulfur

Annealed 900°C for 8hrs with Ammonium carbonate





Discussion

The IR spectra showed similarities between 'without' and urea(3) material between 1704-1168 cm^{-1} (Table 1) There were also differences between 3300-3000 cm^{-1}. 'Without' had a broad OH peak (3166 cm^{-1}) and urea(3) had a broad NH peak (3417, 3184, 3029 cm^{-1}). While the spectrum for thiourea(2) had more variation from 'without' than urea(3). Thiourea had strong coupling of C-N and N-H vibrations (1643, 1577 cm^{-1}) and a broad NH peak (3511, 3412 cm^{-1}).

The PXRD phases identified for tungsten sulfide (WS_2) embedded with thiourea(2) (bottom, 04-003-4880) and without thiourea (top, 04-004-5721) had peak difference between 36-52° 2θ that resulted in a particle size of 5 nm (without thiourea) and 2 nm (with thiourea-2) at 33° 2θ. Overall, WS_2 embedded without thiourea (TU) ranged from 1-5 nm in size compared to 1-2 nm for material embedded with TU2 (Table 2). For material embedded without and with urea(3), the PXRD phase was tungsten nitride ($W_{0.75}N$, 00-064-0678) with a particle size of 1 nm (Table 2).

Scanning electron microscopy (SEM) visually confirmed the particle size of PXRD which was used to observe the material's morphology. WS_2 without the structural directing agent (SDA) thiourea resulted in highly faceted, snowflake-like nanoparticles. With the addition of thiourea, the snowflake-like morphology was retained, but there was a decrease in particle size and an increase in pore volume. Tungsten nitride without urea produced interconnected nanoparticles aggregated into large bundles and comprised of large open pores. Whereas, incorporating urea into the network produced a compact structure with smaller pores. SEM confirmed the particle size results obtained from PXRD for both tungsten sulfide and nitride.

Conclusion

The synthesis of tungsten nitride and sulfide utilizing the sol-gel method and epoxide addition was completed and successfully characterized using IR spectroscopy, powder x-ray diffusion, and SEM. Embedded SDAs, thiourea and urea, successfully altered the surface morphology and particle size when compared to those without SDAs.

Future Work

Further characterization of the material and extensions of the synthesis parameters would allow for the determination of a broader range of the applications. Other possible research involving synthesis with other metal alkoxide aerogels and characterization for alternative applications.

References

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Acknowledgments

I would like to thank the Honors College Undergraduate Research Scholars Program supported by the CH and Helen Jones Foundations, Dr. Louisa J. Hope-Weeks, Vanessa Charles, and the Texas Tech University Department of Chemistry and Biochemistry.