Synthesizing and Printing Tungsten-Doped Vanadium Dioxide Nanoparticles

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Introduction

Vanadium Dioxide

- Metal to Insulator Phase Transition
  - Monoclinic to tetragonal structure change (see Figure 1)
  - Optical and electrical properties shift to reflect IR light and become conductive, respectively
- Tungsten Doping
  - Lower phase transition temperature based on atomic % tungsten
- Ink Formulation and Printing
  - Thermoresponsive optical features and antennas
  - Potential applications in anti-counterfeiting technologies as additional levels of authentication

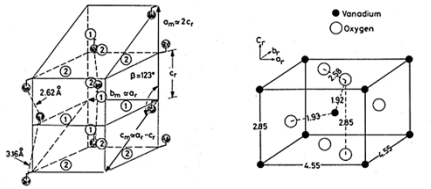

Figure 1: Monoclinic to Tetragonal crystalline structure transition of VO_2[2]

Nanoparticle Synthesis

- 4 M HCl and hydrazine hydrochloride added alternatively to a solution of vanadium pentoxide to yield blue vanadyl chloride
- Vanadyl chloride filtered, mixed with tungstic acid and added dropwise to a sodium bicarbonate solution under nitrogen flow
- Resulting purple solution washed in ethanol and heated in tube furnace at 500 °C for one hour with nitrogen flow to yield crystalline VO_2 (see Figures 2 and 3)

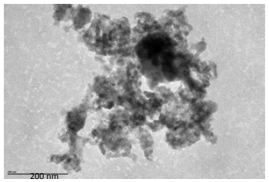

Figure 2: TEM image of doped particles

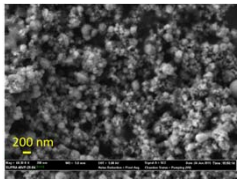

Figure 3: SEM image of doped particles

Results

Synthesis

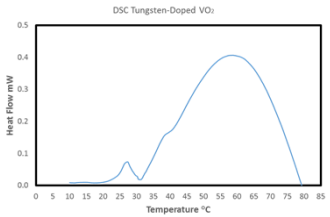

Figure 4: DSC testing of phase transition

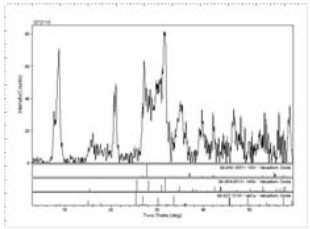

Figure 5: XRD results of doped particles

- SEM and TEM characterization (see Figures 2 and 3) showed doped aggregate particles less than 50 nm in size
- Differential scanning calorimetry testing (see Figure 4) showed an isolated phase transition at 28 °C and a broad phase transition from 30 to 80 °C
- XRD results (see Figure 5) confirm the presence of VO_2, V_2O_5 and other vanadium oxides

Ink Formulation

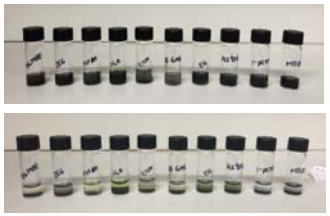

Figure 6: Nanoparticle Dispersion testing

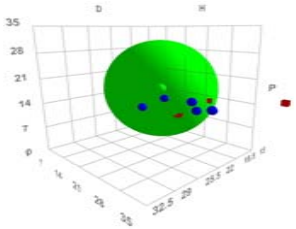

Figure 7: HSPiP solubility space plot

- Particles were dispersed in 10 different solvents: ethylene glycol monobutyl ether, diethylene glycol, methanol, water, ethanol, diethylene glycol hexylether, ethylene glycol, acetone, 1-pentanol and methyl benzoate and left undisturbed for three days (see Figure 6)
- Using the results of the test and the HSPiP solubility parameters program (see Figure 7) (δd: 20.34 δp: 16.95 δh: 14.98, R_0: 14.2), particles were dispersed in a 70/30 solvent mixture of diethylene glycol/acetonitrile

Discussion

TEM and SEM images show particle sizes ranging from 10-200 nm with irregular and non-uniform particle geometries. XRD confirms the presence of additional vanadium oxide species along with VO_2, indicating the need for synthesis refinement. DSC data implies that some particles were doped at 12 atomic % tungsten while there were also concentrations of doped particles at lower atomic %, which indicated an inconsistent tungsten doping. Hansen solubility testing determined efficient solvents for ink formulation would be polar in nature, indicating the need for an aerosol or inkjet printer.

Conclusions

Vanadium dioxide particles can successfully be synthesized and formulated into an ink with a metal to insulator phase transition. Future work will be focused on capping particles with a nonpolar ligand so that they can be dispersed in solvents that are ideal for an aerosol jet printer. An alternative doping source material will be identified to obtain a more consistent phase transition temperature.

References

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2. Zylbersztejn, A., & Mott, N. (1975). Metal-insulator transition in vanadium dioxide. Physical Review B, 11(11), 4383-4395.

Acknowledgments

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