Transparent Thermochromic Smart Window Film





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Project Summary

Timeline:

Start date: April 1, 2019

Planned end date: March 31, 2022

Key Milestones

- 1. Achieved ultra-small M-phase VO2 (<50 nm) via flow synthesis; Feb. 2020
- 2. Demonstrated VO2/PVB smart film; April 2021

Budget:

Total Project \$ to Date:

- DOE: \$1,114k
- Cost Share: \$248k

Total Project \$:

• DOE: \$1,492k

• Cost Share: \$373k

Key Partners:

Florida A&M university

University of Chicago

Lawrence Berkley National Lab

National Renewable Energy Lab

Project Outcome:

This project is to develop advanced energy-efficiency and lowcost VO2 based thermochromic window film by using theoretical simulation and design of films; 2) scalable liquidphase flow synthesis of M-phase VO2 nanoparticles; and 3) scattering-controlled composite thin film manufacturing.

We have successfully accomplished film designs, synthesized M-VO2 with diameter down to 13 nm and demonstrated refractive match coating. The smart film optimum study is under progress. One (1) patent pending, two (2) software and five (5) papers

Team



Dr. Jie Li, PI, Principal Chemical Engineer (ANL)

Expert in advanced materials and process technology, Lead the project and contribute VO2 nanoparticle synthesis using continuous flow hydrothermal reactor, prepare and characterizations of smart films



Dr. Ralph T. Muehleisen, Co-PI, Principal Building Scientist (ANL)

Expert in building science, thermodynamics, and metamaterials for acoustics and vibration. Provide leadership and technical to market guidance as well as knowledge of building construction and performance requirements.



Dr. Bayaner Arigong, Co-PI, Assistant Professor (FAMU)

Arigong is an expert in applied electromagnetic device and transformation optics design, will bring the skills for smart film design including nanocomposite film and metasurface design.



Dr. Matthew Tirrell, Co-PI, Dean and Professor (UC)

Expert in creating novel, functional self-assembled structures focusing on tailored nanomaterials. Contribute to scattering control at VO2/polymer interface in the composite film via refractive index match coating



Dr. Charlie Ćurčija, Co-PI, Scientist V (LBNL)

Expert and leading scientist in the R&D of thermal and optical performance of windows, Provide guidance on the project, contribute energy calculations and characterization of film performance



Dr. Robert Tenent, Material Scientist V (NREL)

Expert in development of new materials for improved electrochemical devices with focus on cost-effective, manufacturing friendly methods for the production of materials for both energy generation (PV) and efficiency (smart windows). Contribute to new film ageing test to the ASTM Standards

Team



Cathy Milostan, Market & Technology Development Analyst

Expert in techno-economic analysis, market assessment, and business development. Work with team on TEA and with Dr. Muehleisen on finding investment and industry partners



Dr. Wei Chen, Chemist, (UC/ANL)

Expert in synthesis of polymeric materials with well-defined molecular weight, microstructure, and functional group; Contribute to functionally graded nano-coatings for engineered VO2/polymer interface for scattering control.



Jacob Jonsson, Principal Scientific Engineering Associate(LBNL) Expert in fenestration optical properties measurement, including solar spectral transmittance, reflectance, as well as complete bi-directional scattering distribution. Contribute on film optical performance characterizations



Dr. Kowsalya Rasamani, Postdoctoral researcher (ANL)

Expert in nano-material synthesis, characterizations. Work with Jie Li on VO2 nanoparticles synthesis, smart film preparation and optical characterizations.



Dr. Kai Mai Tran, Research Aide (Rice University)

Expert in nano-material synthesis, characterizations. Work with Jie Li on high-throughput synthesis of VO2 nanoparticles and material characterizations



Dr. Sovan Banerjee, Postdoctoral Researcher (UC)

Expert in block copolymer synthesis, surface coatings, and characterizations. Work with Matt/Wei on GCP synthesis, coreshell coating, and smart film preparation/characterizations



Elizabeth Rasmussen, Research Aide (University of Washington)

Expert in flow synthesis of MOF materials under supercritical CO2, computer simulation of supercritical fluids. Work with Jie Li on high-throughput flow synthesis of VO2 nanoparticles and VO2 particle characterizations

Challenge



- Advanced windows technologies are required to reduce ~30% energy loss.
- Existing dynamic window film technologies (including electrochromic, thermochromic) have the potential, but are too costly to be widely acceptable.

Concept VO2 Nanocomposite Thermochromic Window Film



Advantages

- Switch adaptively & automatically depending temperature (passive)
- Always allow visible light in
- Save both heating & cooling energy, >18% annually
- NanoVO2 enables high solar energy modulation **and** visible light transmittance
- Potentially more **economic** and affordable due to single active layer structure

Challenge - State of the Art & Technical Gaps





Li et al., J. Applied Phys. 115 (2014) 053513

State of the Art

- Nanoparticle film^{*1} emerges as a breakthrough thermochromic film tech which outperforms conventional bulk film in IR control(Figure left and image right)
- Nanocomposite film shows the best performance versus other material options (figure left upper)

Technical Gaps

- But **conflict** exists between T_{lum} and ΔT_{sol}
- To have high performance smart film, **ultra-small (<50 nm) Mphase** VO2 nanoparticles are required.^{*2}
- NanoVO2 synthesized mostly by the batch reactor method is expensive, poor in quality control with limited scalability.^{*3}
 - Need economic/reliable nanoparticle/film technology



100-300 nm (M) VO₂ crystal size





10-45 nm (M) VO2 crystal size

*1: Li et al. Thin Solid Films, 520 10 (2012); *2: Laaksonen et al. Solar Energy Materials & Solar Cells, 130 132 (2014) *3: \$5.67/g (NN1918 Nano Vanadium Oxide (VO2) Powder from Stanford Advanced Materials, 2020.

Our Approach & Objective

Enable a new generation of smart, high-efficient, low-cost thermochromic dynamic window films

- Approach I: Use the computational method, rather than "trial-and-error", to design/optimize high-performance transparent VO2/polymer films
- Approach II: Demonstrate ultra-small (M) phase VO2 nanoparticles with average diameter < 50nm by developing a rapid scalable continuous flow hydrothermal (CFHT) synthesis, rather than using autoclave, that can synthesize high quality material at reduced product cost
- Approach III: Use RI-matching coating of VO2 to simultaneously enhance visible light transmittance and solar energy modulation
- Objective: Fabricate reliable and repeatable composite films satisfying ASTM E3119/20-17 with T_{lum} > 50%, ΔT_{sol} >15~40% and Tconv ~35°C

Approach I: Theory Analysis

FAMU-FSU College of Engineering

Smart Film – Modeling Theory

-- towards ideal solar modulation and light transmission





Approach II: Material Synthesis (ANL)

Motivation: Nanomaterial is **expensive**! Developing a rapid, scalable modern flow synthesis method using (cheap) water as the solvent is the key to achieve **low-cost VO**₂ & smart film.

✓ Completed: US Patent pending, Feb. 2021, US 9,975,804

Continuous Flow Hydrothermal (CFHT) Reaction under Supercritical H2O



Uniqueness

- Ultrafast reaction (sec. vs days)
- One-step synthesis of crystal structures (no annealing needed)
- Low-dielectric SC water being particularly suited for (high-quality nanomaterials)
 - I. making ultra-small oxide (VO₂) nanoparticles (<50 nm)
 - II. coating organic ligands
 - III. easing particles separation
- Rapidly heating/cooling (for nano VO2)
- □ Simple, "green", fast and scalable process without CO₂ emission
- Feasible automation via ML/AI

Approach III: Controlling VO₂/polymer interface scattering (UC)

Problem: **Trade-off** between visible light transmittance ~ solar energy modulation

Our solution: Design & coat a low-refractive-index (RI 1.3) Gradient Copolymers (GCP) on VO2 particles (RI 3.0) for **effective RI to match RI (1.5) of matrix polymer***

$$\frac{I}{I_0} \sim e^{\frac{-3V_p x r^3}{4\lambda^4} \left(\frac{n_p}{n_m} - 1\right)} \qquad n_p \approx n_m$$

- Apply low refractive index fluorinated polymer (RI ~ 1.33 1.4)
- Assume spherical VO₂ nanoparticles diameter = 50 nm
- Resulting in thickness of grafted polymers is ~ 40 nm.
- Increase compatibility by mixing fluorinated and PMMA with ration of ~40 50% (Note: RI of PMMA ~1.49 and VO₂ ~3.0)

***Our method**: Gradient copolymers of poly(methyl methacrylate) (PMMA) and low-refractive-index poly(perfluoroalkyl methacrylate) (P13FOMA) are identified as a candidate of the VO₂ nanoparticle surface coating.



Impacts

A successful project enables

- **1. optimum design** of VO2/polymer composite films with highest solar modulation, guiding film preparation.
- A "green" and scalable continuous flow hydrothermal (CFHT) process under supercritical water, rather than a batch autoclave, that can rapidly (seconds vs days) manufacture target ultrasmall(<50 nm) m-phase VO2 nanoparticles at low cost;
- 3. A demonstrated **thermochromic film** with T_{lum} > 50% and ΔT_{sol} >15~40% made by a scalable slot-die coater. (with controlled haze,<1% and T_{conv} .)
- 4. A new TC film product with cost controlled < \$12/ft²
- 5. >18% heating/cooling energy saving annually
- 6. Two patents, two software and 4~5 publications

Impacts – Techno-Economic Analysis

Societal Impact:

 Greater energy efficiency(EE) (>\$18% annual heating/cooling savings) by reducing energy loss from windows to support net zero energy buildings and global mandates for de-carbonization

Technology & Market Impact:

- Technology competitive advantages: higher visibility plus dynamic energy savings at lower cost (< \$12/ft²) than low-e films (~\$15/ft²) and current thermochromic films (~\$30-\$50/ft²)
- Building owners & consumers: lower costs for shorter paybacks than low-e films (low-e films re-install issues & longer paybacks, especially in northern climates)
- Window film vendors & manufacturers: opportunities to enhance solar films with more heat reduction & visible light transmission (3M Prestige50(50% VLT) & Night Vision(15%-35% VLT)).

Value Proposition:

Argonne used nano technology to develop thermochromic smart window films with higher transparency & greater reduction in winter heat loss/summer heat gain (at a lower cost than 'low-e' window films) to deliver >18% annual heating/cooling energy cost savings for building owners & consumers

Progress I: Theory Analysis (Composite film & design tool)

- Modeling theory is developed to characterize the optical property of smart film composed of VO2 nanoparticles
- Optimization algorithm is developed to improve the solar modulation and transmission
- Two publications: 1 journal paper (Applied Physical Lett.)
 2 conference paper (CLEO)

- **Design tool** is developed for film performance analysis
- Software has been compiled to calculate optical properties.
- More options applying different methods will be integrated





Input Option Wavelength Range in nm lower limit 200 upper limit 2500	S Material Type metallic, E parallel metallic, E parpendicular metallic, E perpendicular semiconducting, E perpendicular metallic, film semiconducting, film	Particle Type • spherical oriented prolate oriented oblate random prolate core-shell	Filling Factor Aspect Ratio Matrix Dielectric Constant Core Dielectric Constant	0.01 1 1.5 2	V (x/t) d1 (nm) d2 (nm) Substrate Refractive Index	1 1e+04 0 n: 1.5 k: 0
X axis • wavelength frequency • energy	Sa Sa	ave Inputs IVE				
Case • 1 layer 2 thin layers thin/thick layers particle stack	Options Luminous Ti Luminous Solar Ti Sola Sola NIR Sola File Name	ransmittance: 58.72 Reflectance: 1.50 ransmittance: 45.38 Reflectance: 1.37 ar Modulation: 25.72 ar Modulation: 40.16	45684 02011 07829 52139 06212 66624		ave Inputs	

Progress I: Energy Saving Calculation Tool (LBNL)

Energy savings by climate and thermochromic parameters

- Range of potential thermochromic parameters:
 - Glazing configurations: 5
 - Dark state transmittance: 4
 - Light state transmittance: 3
 - Transition temperature: 4
 - Climates: 5
 - Orientations: 4
 - Lighting controls: 2
 - Surface number: 2
 - Total runs: 19,200 plus 200 baseline runs for comparison
- 3 separate sets of surface plots showing total energy consumption and energy savings:
 - Tsol(low) vs Transition Temperature
 - Tsol(hi) vs Transition Temperature
 - Tsol(low) vs Tsol(hi)



Impact of COVID 19 on experiment work

 Experimental work has been significantly affected by COVID-19 locking down, we have no or limited access to the Lab.

We have been managing to generate as much data as possible.

Most work focused on VO2 nanoparticle synthesis, and smart film research started from January 2021

Progress II: Pure M-Phase VO2 Nanoparticles Synthesized, <50 nm

✓ Demonstrated it is feasible to obtain high-quality of 1) uniform and 2) small (<50 nm) and 3) M-VO2 using our CFHT tech.</p>



Progress II: Optical Performance (Pristine VO2@PVB films)

 Optimum solar modulation exists in certain domain of 1) film thickness and 2) VO2 load, which depends on VO2/polymer interface.







Progress II: Applying Capping Method (Adding More Functions)



Progress III: Synthesis of GCP & GPC Characterization



Progress III: RI-match performance of GCP-Coated VO2/PMMA Films

Parametric studies of varying GCP-coated VO₂@SiO₂ particle concentrations & coating thickness
 ✓ confirms that GCP coating efficiently matches the RI of the VO₂ particles with dispersion matrix ~range=1.55-1.60.



TEM of GCP coated VO₂@SiO₂



Progress: Outcome up to date (Project is in Mid-Stage)

- Patent (1): "PROCESS FOR RAPIDLY MANUFACTURING ULTRASMALL PHASE-CHANGE NANOMATERIAL", #IN-20-095 (ANL), 0003-3732 (Cherskov), US Patent application, submitted Feb. 2, 2021. (selected by TDC Argonne National Lab.)
- Papers (5): Ren, et al., "A patterned phase-changing vanadium dioxide film stacking with VO2 nanoparticle matrix for high performance energy-efficient smart window applications," Applied Phys. Lett., 118 (2021)051091.
 - ✓ Tran, et al., "High throughput screening synthesis of vanadium (IV) oxide nanoparticles using supercritical water in a continuous flow hydrothermal reactor", submitted to Crystal Design and Growth, May 2021, in revision.
 - ✓ Hassna, et al., "Inverse design inspired VO2 smart window film," Conference on Lasers and Electo-Optics (CLEO), 2021.
 - Sanerjee et al., "VO₂/polymer Based Smart Inorganic Hybrid Thermochromic Window Coating: Design Strategy, Recent Progress and Future Prospect", in preparation for **Progress in Polymer Science**.
 - ✓ Banerjee et al., "Match Refractive Index of VO2 Nanoparticles with PMMA matric using Fluorinated Gradient Copolymers", in preparation for **Polymer Chemistry**.
- **Software (2):** 1) Optical design of nanocomposite thermochromic films (Frank, Bayaner, 2020); 2) Energy calculation of thermochromic films (Curcija, LBNL, May 2021)
- Presentations (3): Rasmussen, at al., "Supercritical Water Flow Influence on Synthesizing Uniformly Sized Nanoparticles" paper presented at the 73rd Annual Meeting of the APS Division of Fluid Dynamics, Nov. 22, 2020. Published in APS Division of Fluid Dynamics, American Physical Society, Fall 2020.
 - Spurling RJ, et al., Res. and Dev. of Energy-Saving Smart Windows for the Next Generation of Green Buildings. Invited talk. Univ. of Tennessee Honors & Scholars Lecture Series. 2020, Oct. 16. Knoxville, TN, USA.
 - Spurling RJ, et al., Supercritical Synthesis of VO₂ Nanoparticles for Smart Window Films. Poster presented at: a) Materials Science & Technology; 2020 Nov. 2-6; b) Microscopy & Microanalysis Congress for Students, Post-Docs, and Early Career Professionals; 2020 August 3

Awards (2): 2nd Prize, Oak Ridge Chapter of ASM Annual Student Poster Competition, Undergraduate Division (Jackson Spurling); 3rd Prize, Materials Science & Technology Conference Student Poster Competition, Undergraduate Division (Jackson Spurling)

Remaining Work: Film optimization + scale-up



DA-CAPPED VO2 FILM shows improved transparency. Its optical modulation is under investigation

- 1. Correlate theory and experiment and optimize solar modulation using **inverse design**
- **2.** Increase solar modulation by using surface modified VO₂ by organic ligands;
- Reduce VO₂ conversion temperature and control film color by doping element (W, Mg, Sn, 68°C to 35°C);
- Conduct optical (LBNL) and ageing tests (NREL) of smart films to Standard ASTM E3119/20-17 to confirm suitability/durability of PVB matrix and PET substrate materials;
- 5. Finalize **energy saving calculations** of our final TC films using LBNL newly developed software.

Stakeholder Engagement (Project is in Mid-Stage)

- **Stage:** Project is in the **middle** stage of development
- Scale-up: Talked with Corning Advanced Flow reactor for material process scale-out/up
- Pilot: Coordinating with Cardinal Coated Glass and 3M to enable large area of smart film by conducting the pilot and commercial scale roll-to-roll film preparation using their exiting coaters and characterize film performance during the maturation stage to expedite development;
- Field testing: Franklin Energy/Argonne Lab will be willing to support for field test and demonstration
- Techno-economic analysis (TEA): continuing TEA with experimental data & customer discovery to identify market growth, competitive niches, early adopters & beta testers
- DOE TCF is supporting on process scale-up to manufacture enough VO2 materials for making large area of smart films

Thank You

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REFERENCE SLIDES

Project Budget

Project Budget: \$1,492,026 for FY19 - FY22. Variances: No budget variances Cost to Date: \$1,114,00 (75%) Additional Funding: \$250k TCF from OTT/DOE

Budget History										
Apr. 2019 (p	– FY 2020 ast)	FY 2021	FY 2021 (current)		Apr. 2022 nned)					
DOE	Cost-share	DOE	Cost-share	DOE	Cost-share					
725k	181k	420k	105k	347k	87k					

Project Plan and Schedule

Project Schedule												
Project Start: April 2019		Completed Work										
Projected End: April 2022		Active Task (in progress work)										
		Milestone/Deliverable (Originally Planned) use for missed									issed	
		Milestone/Deliverable (Actual) use when met on time						e				
		FY2019-20				FY2021				FY2022		
Task	Q3 (Apr-Jun)	Q4 (Jul-Sep)	Q1 (Oct-Dec)	Q2 (Jan-Mar)	Q3 (Apr-Jun)	Q4 (Jul-Sep)	Q1 (Oct-Dec)	Q2 (Jan-Mar)	Q3 (Apr-Jun)	Q4 (Jul-Sep)	Q1 (Oct-Dec)	Q2 (Jan-Mar)
Past Work												
T1 Ultra-small VO2 nanoparticle synthesis: - Average VO2 diameter <50 nm												
T2 Theory for cloaking VO2												
T3 Energy modeling												
T4 VO2/Polymer composite film LT>60%; Tsol > 15% ~ 40%									•			
T5 Milestone: VO2@matrix RI matchingcoating									•			
Current/Future Work												
T6 Film optimization via surface coating												
T7 tuning film color@ conv. temp. via dopping												
T8 Film perfomance@ageing test												
T9 T2M activities												