Elucidating the Crystallite Size Dependence of the Thermochromic Properties of Nanocomposite VO₂ Thin Films

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Supporting Information

ABSTRACT: Fenestration elements that enable spectrally selective dynamic modulation of the near-infrared region of the electromagnetic spectrum are of great interest as a means of decreasing the energy consumption of buildings by adjusting solar heat gain in response to external temperature. The binary vanadium oxide VO₂ exhibits a near-room-temperature insulator—metal electronic transition accompanied by a dramatic modulation of the near-infrared transmittance. The low-temperature insulating phase is infrared transparent but blocks infrared transmission upon metallization. There is considerable interest in harnessing the thermochromic modulation afforded by VO₂ in nanocomposite thin films. However, to prepare a viable thermochromic film, the visible-light transmittance must be maintained as high as possible while maximizing thermochromic modulation in the near-infrared region of the electromagnetic spectrum, which necessitates the development of high-crystalline-quality VO₂ nanocrystals of the optimal particle size embedded within the appropriate host matrix and refractive index matched to the host medium. Here, we demonstrate the preparation of acrylate-based nanocomposite thin films with varying sizes of embedded VO₂ nanoparticles. The observed strong size dependence of visible-light transmittance and near-infrared modulation is explicable on the basis of optical simulations. In this article, we elucidate multiple scattering and absorption mechanisms, including Mie scattering, temperature-/phase-variant refractive-index mismatch between VO₂ nanocrystals and the encapsulating matrix, and the appearance of a surface plasmon resonance using temperature-variant absorptance and differential refractive-index scattering performed as a function of particle loading for the different sizes of VO₂ nanocrystals. Nanocrystals with dimensions of 44 ± 30 nm show up to >32% near-infrared energy modulation across the near-infrared region of the electromagnetic spectrum while maintaining high-visible-light transmission. The results presented here, providing mechanistic elucidation of the size dependence of the different scattering mechanisms, underscore the importance of nanocrystallite dimensions, refractive-index matching, and individualized dispersion of particles within the host matrix for the preparation of viable thermochromic thin films mitigating Mie scattering and differential refractive-index scattering.

INTRODUCTION

Buildings account for an inordinately large amount of energy consumption across the planet and are often static structures that remain unchanged in the face of changing seasons and diurnal temperature variations.1 A recent report from the United Nations estimates that 30–40% of primary energy usage across the world occurs within buildings.2 In the United States, the Department of Energy estimates that 41% of the total energy consumption can be attributed to buildings.2,3 Much of the energy consumed within buildings goes toward space cooling, space heating, lighting, and ventilation. Incorporating responsive elements that can adapt to external stimuli (e.g., external temperature and humidity) within structural elements has been proposed as a potential means of reducing the energy footprint of buildings.4,5 Fenestration elements, such as windows, doors, and skylights, play an important role in determining the solar heat gain of a building. Such elements must balance the competing needs of enabling interiors to be lighted using natural daylight while modulating solar heat gain to acceptable levels. Consequently, there is great interest in the development of spectrally selective thin films that allow for transmission of visible light while enabling...
dynamical modulation of infrared transmittance in response to the external temperature. Such thin films are expected to bring about substantial energy savings by blocking infrared light during periods of high ambient temperature (thereby reducing the need for space cooling) but permitting transmittance of infrared light during periods of low ambient temperature when the solar heat gain can be harnessed to reduce heating costs. Nearly 45% of the total solar energy in the range between 400 and 2500 nm corresponds to near-infrared radiation (780–2500 nm); consequently, a reduction in the solar flux in the near-infrared region would drastically reduce the transmitted energy associated with solar heat gain.

Dynamically tunable glazing requires stimuli-responsive modulation of optical transmittance, which can be achieved variously by means of thermotropic or lyotropic phase transitions in polymers or hydrogels, electric-field-induced ion intercalation in redox-active host materials, reversible amorphous-to-crystalline transitions in phase-change materials, electric-field-induced change of polarization of liquid crystals, or electronic solid–solid phase transitions.1,2,9–14 Thermochromic transitions are particularly important as a facile means of developing dynamically switchable glazing that does not require external voltage control.15 Compounds that exhibit amorphous-to-crystalline transitions in phase-change materials, electric-field-induced change of polarization of liquid crystals, or electronic solid–solid phase transitions are particularly attractive.15–19 However, there exists only a relatively sparse set of compounds characterized by large thermally induced modulations of electrical conductance; such electronic phase transitions are underpinned typically by either electron correlation or electron–phonon coupling.18,19,21–24 The binary vanadium dioxide (VO$_2$) is notable in having an electronic phase transition that occurs in close proximity to room temperature.19,25 In the bulk, the metal–insulator transition of VO$_2$ is observed at ca. 67 °C but can be depressed through size control or the incorporation of substitutional/interstitial dopants.17,26–32 The underlying origin of the transition remains hotly contested given that the transition has both electronic (Mott–Hubbard) and structural (Peierls') attributes.19,28,33–35 Regardless of the fundamental origin of the transition, the dramatic modulation of optical transmittance and electrical conductivity observed at the phase transition makes VO$_2$ a useful material for practical applications.

For deployment of VO$_2$ within thermochromic thin films, wherein it can be integrated within various parts of the building envelope,3,10,36 three compelling requirements must be addressed: (a) the luminous transmittance (a quantitative measure of light in the region visible to the human eye) must be maintained as high as possible while maximizing thermochromic modulation in the near-infrared region of the electromagnetic spectrum; this requires mitigation of various light scattering mechanisms (vide infra); (b) the thin film must be thermally cyclable without strain-induced cracking; the substantial lattice strain accompanying the structural phase transformation renders the deployment of continuous thin films rather difficult and instead nanostructures embedded within suitable matrices are better able to accommodate such strain;17–30 (c) the nanocrystallites need to be well dispersed within the host matrix to prevent light scattering and to ensure retention of mechanical integrity of the film across multiple thermal cycles. It is thus expected that a viable thermochromic thin film will comprise high-crystalline-quality VO$_2$ nanocrystals of the optimal particle size embedded within the appropriate host matrix.10–33 Some notable efforts in the literature, such as by Chen et al., have resulted in Δ$T_{\text{vis}}$ the modulation in transmittance from 400 to 2500 nm, reaching as high as 19.1% when VO$_2$ is encapsulated in ZnO.44 Values of $T_{\text{lum}}$, luminous transmittance in the 400–780 nm range, as high as 62.1% have been demonstrated by Zhang et al.45 through grinding of VO$_2$ particles. However, fundamental mechanistic understanding of the influence of different scattering mechanisms on the thermochromic performance of nanocomposite films remains to be elucidated.

Previous work has shown that high-crystalline-quality VO$_2$ nanocrystals are accessible through low-temperature hydrothermal methods.26,27,46,47 Such methods provide substantial control over particle size and dopant incorporation; the obtained nanostructures can be extensively thermally cycled without cracking. In past work, we have incorporated hydrothermally grown VO$_2$ nanowires within an amorphous silica matrix utilizing a modified Stöber method.48 The silica matrix permits adhesion to glass substrates and provides protection against oxidation. VO$_2$ particles have further been used in other studies to prepare nanocomposite thin films using polymer-assisted deposition and through mixing with an acrylic resin.49,50 However, the first and third of the problems noted above, optimal particle size and good dispersion, remain to be adequately resolved. Here, we contrast the visible-light transmittance and infrared modulation obtained for different particle sizes of VO$_2$ embedded within a commercially available methacrylic acid/ethyl acrylate (MAA/EA) copolymer, Acrysol ASE-60. The rheology of this matrix enables the use of drawdown coating for the preparation of nanocomposite VO$_2$ thin films. Films formulated with four different sizes of VO$_2$ nanocrystals at various mass loadings have been examined; a detailed evaluation of light scattering mechanisms occurring within the nanocomposite thin films underscores that a combination of both nanometer-sized dimensions and excellent dispersion at the crystallite level (without agglomeration as particles) is imperative to obtain the desired high degrees of visible-light transmittance and thermochromic modulation.

### RESULTS AND DISCUSSION

The use of nanocrystals instead of continuous thin films provides several key advantages. First, as noted above, strain-induced delamination and cracking of continuous thin films resulting from the lattice mismatch at the monoclinic–tetragonal structural phase transition can be mitigated.16,26 Second, nanocrystals embedded within flexible polymeric thin films serve as retrofittable solutions, providing a means of readily modifying existing solar control films, and thus can be deployed onto existing buildings without requiring replacement of insulating glass units in their entirety. Finally, nanocrystals can be prepared in a highly crystalline form by scalable solution-phase methods and do not require high-vacuum deposition chambers necessary for physical vapor deposition of VO$_2$.51 However, the utilization of nanocrystals within optical quality thin films brings its own set of challenges associated with determining the optimal crystallite size and ensuring good dispersion of VO$_2$ nanocrystals within matrices so as to mitigate light scattering arising from the agglomeration of crystallites.

Li et al. have suggested a pronounced size dependence for the optical transmittance and near-infrared modulation of VO$_2$.
nanocrystals embedded within a dielectric matrix. These authors have found that nanocomposite films constituted by dispersing spherical- and elliptical-shaped VO₂ nanocrystals present several advantages over continuous thin films of VO₂. First, the spectral transmittance of the insulating phase of VO₂ is predicted to be much higher for films with VO₂ nanocrystals dispersed within a matrix as compared to that of continuous thin films. In addition, the near-infrared modulation for the particulate thin films was further found to be substantially greater than that of the continuous thin films. To elucidate the crystallite size dependence of the optical properties, simulations have been performed using effective medium approximation (EMA) and finite element analysis + geometrical optics (FEA + GO) models (Figure 1). The simple EMA approach assumes that the nanoparticle has a single refractive index (n) and extinction ratio (k) and assumes that the particles are homogeneously distributed throughout a low-n medium (Figure 1A). The simulated spectrum (Figure 1B) predicts a dramatic modulation at a maximum of ca. 40% in the near-IR region of the electromagnetic spectrum when using the optical constants of bulk VO₂ in the monoclinic (M1) and tetragonal phases. The simulation assumes a constant n of ca. 1.5 for the host matrix, which is typical of polymeric media. The FEA + GO simulations allow for a more detailed elucidation of particle-size-dependent optical properties. Spectra have been simulated for a composite with a fill factor of 3.7 wt % of spherical VO₂ nanoparticles of varying diameters as labeled in the plot in the insulating and metallic phase. As the diameter increases from 20 to 100 nm, the near-infrared modulation is observed to remain constant at ca. 40% (Figure 1C). However, the maximum visible-light transmittance (at 680 nm) decreases from 80 to 68% for the low-temperature phase. When considering a composite of 100 nm long VO₂ nanowires with varying diameters, the 50 and 100 nm diameter nanowires show a maximum modulation of ca. 45% in the near-infrared region of the electromagnetic spectrum, whereas the 20 nm nanowires are predicted to exhibit a maximum modulation of ca. 40% (Figure 1D). Although the NIR modulation is slightly diminished for the 20 nm diameter nanowires, they retain superior visible-light transmittance. The substantial diminution in visible-light transmittance with increasing particle size is derived from the scattering background contributed by larger particles. Agglomeration of particles will to first order mimic the effects of having larger particles. A reduction in n from 3.0
to 2.2 at 700 nm when transitioning from an insulator (M1) to metal (R) is also responsible for an increase in visible transmission in the metal phase, but this change is constant between films and has little impact on variations in film performance.55,56 These simulations indicate that the viability of utilizing VO₂ nanocrystals for effective thermochromic modulation will depend sensitively on their dimensions and extent of dispersion within the host matrix.

To experimentally study the effects of particle size on the optical spectra of the nanocomposite films, VO₂ nanocrystals have been synthesized using different hydrothermal methods, as detailed in the experimental section.26,57,58 Four different particle sizes are examined here: sample I consists of nanowires prepared by the hydrothermal reduction of V₂O₅ by 2-propanol, spanning 210 ± 70 nm in diameter and ranging tens of microns in length, as shown in Figure 2A.46 The use of acetone as a reducing agent yields nanowires that again span several micrometers in length but with reduced diameters of 180 ± 70 nm (Figure 2B). These samples are referred to as sample A. To reduce the longitudinal dimensions, the nanowires of sample I have been dry-milled with methacrylate polymer beads to obtain sample I-BM (Figure 2C). Ball-milling greatly diminishes the particle width to 110 ± 90 nm, but the nanocrystals are observed to be highly agglomerated and some amorphization of the crystallites is discernible. Histograms of size distributions obtained from statistical analysis of transmission electron microscopy (TEM) images have been documented in our previous work.29 Finally, to achieve VO₂ nanospheres with an approximate size distribution of 44 ± 30 nm, VO(OH)₂ is first precipitated using sol–gel techniques, followed by hydrothermal crystallization (referred to as sample NS, Figure 2D).57,58 The synthesis of VO₂ NS by hydrothermal methods from reduction of pentavalent vanadium precursors has been reported in a previous work by Zhou, Jin, and co-workers.58 Size heating- and cooling-phase transitions for each of these samples is shown in Figure S1 (Supporting Information). Heating transition temperatures for I, A, and I-BM samples are between 66 and 70 °C, comparable to those of bulk VO₂, whereas the NS sample transitions slightly lower at 57 °C likely due to surface effects, as delineated in previous works.46,59,60 Scaling to finite size diminishes the transition temperature of both the heating and cooling transitions of VO₂; surface-nucleation mechanisms allow for the monoclinic → tetragonal transformation to be initiated at lower temperatures upon heating; in contrast, the cooling transition is mediated by point defects and is suppressed as a result of the lower density of nucleation sites.60 Nucleation restrictions for smaller particle volumes (smaller nanocrystals allow for more facile migration of oxygen vacancies to surfaces, thereby diminishing the density of putative nucleation sites) bring about an increase in hysteresis, as observed in Figure S1.58–61 Notably, the large hysteresis resulting from a reduced concentration of nucleation sites renders crystalline particles with much smaller dimensions of limited practical utility for thermochromic applications. Figures S2 and S3 (Supporting Information) exhibit powder X-ray diffraction (XRD) patterns and selected area electron diffraction (SAED) patterns acquired for the nanoparticles.
Figure 3. Schematic illustration of the process used to prepare nanocomposite thermochromic elements. (A) (1) V2O5 powder is placed in a hydrothermal vessel with deionized water and the reducing agent of choice (either acetone to yield sample A or 2-propanol to obtain sample I). The solution is heated at 210 °C for 18–72 h. (2) Vacuum filtering and washing of the retrieved VO2. (B) followed by (3) annealing of retrieved VO2 under argon to obtain nanowires in the M1 phase. (4) Retrieval of M1 VO2 nanowires followed by (5) dry-milling with methacrylate polymer beads to reduce size (sample I-BM) followed by (6, 7) coating with a SiO2 shell to minimize aggregation, providing gradation of refractive indices, and obtaining VO2@SiO2 nanocrystals. Panel (B) shows the process for synthesis of VO2 NS. (1) Reaction that results in precipitation of amorphous VO2. (2) Hydrothermal treatment of amorphous VO2 to obtain NS crystallized in the M1 phase. (3) Filtering and washing of M1 VO2 NS followed by (4) coating with a SiO2 shell to obtain VO2@SiO2 nanocrystals. Panel (C) outlines the film casting process beginning with VO2 dispersion in an aqueous solution methacrylic acid/ethyl acrylate copolymer followed by (1) casting of films by depositing the dispersion on a borosilicate glass substrate and drawing a casting knife down along the surface to create an even film. (2) Curing for 12 h to obtain a homogeneous nanocomposite film.

used in this study, respectively, confirming that they crystallize in the monoclinic M1 phase. The SAED patterns attest to the single-crystalline nature of the VO2 nanowires; a combination of discrete diffraction spots and diffuse rings are observed for the NS samples as a result of their agglomeration within polycrystalline aggregates. Extensive Raman spectroscopy characterization of hydrothermally prepared VO2 nanowires has been published in our previous work. The hydrothermal methods are documented to yield high-crystalline quality VO2 nanocrystals exhibiting abrupt 4 orders of magnitude changes in conductance in single-nanowire electrical transport measurements. The four samples examined here provide an effective means for elucidating particle size effects on visible-light transmittance and near-infrared modulation of nanocomposite thin films. Notably, the focus of this article is the elucidation of crystal size effects on thermochromic performance for well-characterized nanostructures with varying dimensions with a particular emphasis on examination of the size dependence of light scattering mechanisms; consequently, parameters pertaining to the encapsulating matrix (dielectric shell thickness, surface functionalization of shells, and choice of polymeric matrix, as will be discussed below) have been held constant while varying particle size. All of these parameters can undoubtedly be further improved to enhance functional performance.

Our previous work has illustrated the importance of protecting the VO2 nanocrystals from oxidative degradation by deposition of amorphous silica shells. The silica shells do not alter the magnitude or phase transition temperature but passivate the surfaces of VO2, endowing stability up to temperatures of 300 °C, allow for much improved dispersion in aqueous media, and facilitate refractive-index matching (the refractive index of SiO2 is 1.8 for amorphous SiO2 thin films, intermediate between that of the embedded VO2 nanocrystals and the host polymer matrix (ca. 1.5)). In the absence of a SiO2 coating, VO2 nanocrystals dispersed in aqueous media are rapidly degraded to green substoichiometric vanadium oxides (such as V3O11) and orange V2O5. All four samples noted above have been coated with SiO2 using a modified Stöber approach. In previous work, we have demonstrated the functionalization of SiO2 shells with perfluorinated silanes, which further renders the nanocrystals superhydrophobic and ensures their long-term preservation at high relative humidities. However, this additional treatment has not been performed here to maintain well-defined interfaces with gradation of refractive indices (VO2/SiO2/polymeric medium). Figure 2EF depicts representative TEM images of silica-coated VO2 nanocrystals, indicating an average shell thickness of 4.0 ± 0.6 nm following the procedure described in the Methods section. To devise a scalable process for casting thin films of VO2 nanocrystals, a methacrylic acid/ethyl acrylate (MAA/EA) copolymer is used as a dispersant and thickener. The polymeric matrix is typically stored under acidic conditions; upon titration of a base, methacrylic acid groups within the copolymer become deprotonated and take on an anionic charge. Charge repulsion between anionic groups induces swelling of the copolymer, substantially modifying the rheology of the dispersion and allowing for stabilization of solution-castable dispersions of VO2@SiO2 nanocrystals. Figure S4A (Supporting Information) illustrates MAA/EA copolymer dispersions of VO2@SiO2 nanocrystals allowed to stand for up to 7 days after mixing. Figure S4B contrasts the stability of
the VO$_2$@SiO$_2$ colloidal dispersions in deionized water, with and without the addition of the MAA/EA copolymer, as a function of time clearly illustrating the decreased sedimentation obtained for the dispersion where the polymer is present.

The viscous acrylic dispersions have been used to cast VO$_2$ nanocomposite coatings using a facile straight-edge knife casting process. Figure 3 shows a process flow diagram for the preparation of the nanocomposite thermochromic elements. The obtained films are visually transparent and smooth, as depicted in Figure S4C−F of the Supporting Information. As expected and discussed in greater detail below, the nanocomposite films embedded with the smallest particles show the least amount of haze and the highest optical transmittance in the visible region of the electromagnetic spectrum owing to the most effective mitigation of light scattering. For the same VO$_2$ nanocrystal loading (0.6 mg VO$_2$@SiO$_2$/mL solution), it is clear that the nanowire samples with larger dimensions (samples I, A, and I-BM) show considerably greater haze as compared with the NS nanocrystals, indicating different absorption/scattering wavelength profiles.

Visible−NIR transmission spectra of nanocomposite films prepared using the four VO$_2$@SiO$_2$ samples are shown in Figure 4. The corresponding transmittance and NIR modulation values are listed in Table 1. Three different nanocrystal loadings have been contrasted in each instance. The visible-light transmittance is diminished in each case with increasing loading indicating higher absorption and scattering events within the nanocomposite matrix, the former as a result of the higher optical density resulting from the increased fill factor and the latter as a result of increasing agglomeration of crystallites or primary articles (vide infra). All spectra show a clear divergence of the high-temperature (dotted line) spectrum from the low-temperature (solid line) spectrum in the NIR region of the electromagnetic spectrum. The insulating phase of bulk VO$_2$ has a band gap estimated to be ca. 0.6 eV, whereas with closing of the band gap and sharp increase in carrier density upon metallization, the transmittance is greatly diminished in the NIR region of the electromagnetic spectrum. For samples I and A, with the largest dimensions of nanocrystals under consideration, four correlated observations point the operation of multiple scattering mechanisms: (a) the intriguing observation of higher visible-light transmittance ($T_{\text{lum}}$) at high temperatures and (b) decreased transmission for sample A compared to that of I for any given loading, (c) relatively greater near-infrared modulation ($\Delta T_{\text{NIR}}$) for A as compared to that of I for any given loading, (d) a pronounced blue-shift in onset wavelength of $\Delta T_{\text{NIR}}$ for sample A in comparison with sample I.

The first and most notable observation is the significant increase in $T_{\text{lum}}$ at higher temperatures and is explicable considering the change in $n$ of the VO$_2$ nanocrystals as a result of the insulator−metal phase transition. The value of $n$ at 700 nm for VO$_2$ is 3.0 for the M1 phase and 2.2 for the R
Table 1. Collated Data Summarizing ΔTsol (%), ΔNIR (%), Encapsulated within SiO2 Shells for Various Particle Loadings Dispersed in an Acrylate Matrix

| sample size in nm | 4 mg/10 mL | 6 mg/10 mL | 8 mg/10 mL | 1660 nm | 1380 nm | 1150 nm | 1380 nm | 1380 nm | 1380 nm |
|-------------------|------------|------------|------------|---------|---------|---------|---------|---------|---------|
| I (210 ± 70)     | 2.8        | 2.0        | 1.6        | 1.9     | 1.3     | 1.1     | 1.3     | 1.3     | 1.3     |
| A (180 ± 70)     | 0.9        | 1.3        | 1.0        | 4.6     | 4.4     | 4.0     | 4.4     | 4.4     | 4.4     |
| BM (110 ± 90)    | 1.5        | 0.2        | 0.3        | 6.1     | 5.2     | 3.2     | 5.2     | 5.2     | 5.2     |
| NS (44 ± 30)     | 10.3       | 6.2        | 3.2        | 10.3    | 6.2     | 3.2     | 10.3    | 6.2     | 3.2     |

ΔTlam (%), ΔTlam (%), and Onset of NIR Modulation for the Four Different Size Distributions of VO2 Nanocrystals Encapsulated within SiO2 Shells for Various Particle Loadings Dispersed in an Acrylate Matrix

phase,\textsuperscript{55,56} which results in a greater Δn mismatch between VO2 and the MAA/EA copolymer host matrix at low temperatures. The SiO2 shell with an intermediate n value of 1.8 facilitates refractive-index matching between the embedded nanocrystals and the host matrix,\textsuperscript{63,64} thereby serving as an antireflective coating and minimizing light scattering at the VO2/MAA–EA copolymer interface depending on shell thickness. In this study, the shell thicknesses have been held constant for all of the four nanocrystal sizes. The differential in refractives of the two phases gives rise to an increased scattering component for the low-temperature phase that is reflected as a negative ΔTlam value in Table 1; accordingly, there is no significant change in magnitude as a result of nanocrystal loading for either of these two samples. From a practical perspective, the negative term strongly effects the overall full-spectrum Tsol performance values (Table 1), effectively negating any gains in energy efficiency derived from ΔTlam given the higher weighting of the visible region in the AM1.5 spectrum. The second and third observations related to a decrease in overall transmission and increase in NIR modulation between samples A and I go hand-in-hand and return to the intrinsic trade-off of VO2-based thermochromic elements: increasing the loading of VO2 increases the NIR modulation but also decreases visible transmission. In this comparison, the amount of VO2 within a given loading is constant but owing to the substantial change in morphology (thick nanowires as compared with thin ribbons) between samples, the absorption cross section is much higher for the ribbonlike sample A (note the lack of additional light scattering, as delineated by similar ΔTlam values in Table 1). Although this effect is not drastic from a numerical performance standpoint, the observation does highlight an additional morphology effect not accounted for in the above theoretical models. The final observation is the 280–350 nm blue-shift of the NIR modulation onset wavelength between samples A and I (Table 1). The inflections between high- and low-temperature spectra for samples I and A are observed at ca. 1660 and 1380 nm, respectively. The shift to shorter wavelengths is a result of smaller Mie scattering contributions as a result of the reduced size of the nanowires in sample A. These modulation onsets are clearly unviable for fenestration applications since the solar flux beyond this wavelength is minimal.

The rather poor performance metrics of samples I and A is explicable on the basis of the simulations in Figure 1. The low Tlam and ΔTlam values, coupled with long-wavelength NIR modulation onsets, clearly indicate a size-dependent light scattering mechanism. Mie scattering in the visible–NIR region becomes significant when the diameter of the particle is comparable to or greater than the wavelength of the interacting photon, resulting in a scattering in the forward direction. With this in mind, we have examined I-BM and NS samples that have particle dimensions well below the 400–2500 nm range of the visible–NIR spectrum (Figure 4C,D). Notably, the I-BM sample displays a substantial improvement in ΔTlam; however, the ΔTsol values are still offset by a significant negative ΔTlam component (Table 1). Interestingly, the amount of light scattering in the visible region of the electromagnetic spectrum, characterized by ΔTlam, is significantly larger than that of the I and A samples. In contrast, the NS samples do not exhibit a scattering background. A significant increase in Tlam along with a substantial enhancement of ΔTlam is deduced from the spectra of the NS.
nanocrystals (Figure 4D) and is clearly manifested in the performance metrics enumerated in Table 1. These samples exhibit ΔT\NIR values as high as 32.18% with ΔT\sol values greater than 16% at high loadings. The improved visible-light transmittance can be attributed to the reduction of Mie scattering, whereas the improved ΔT\NIR performance can be traced to the formation of a localized-surface plasmon resonance (LSPR) with a maximum absorbance between 1200 and 1400 nm for particles sub 100 nm in size. The LSPR wavelength is advantageous for thermochromic fenestration purposes as the onset of the resonance begins close to the visible−NIR crossover point in the solar spectrum. A fraction of the I-BM nanocrystals is also expected to be within the size regime wherein LSPR formation is expected.66 However, the NIR onset for I-BM samples is deep in the NIR region of the electromagnetic spectrum, which in conjunction with low T\lum values comparable to those of I and A samples and a significantly increased ΔT\lum suggests an "effective" particle-size-dependent scattering mechanism is manifested owing to the agglomeration of the I-BM nanocrystals to form larger particles.

Specular transmission data shown in Figure 4 provide vital optical performance metrics but provide limited mechanistic insight into optical processes such as scattering, reflection, and absorption within the nanocomposite films that underpin these metrics since all of these parameters are incorporated within the measurement of a singular intensity value at each wavelength. To derive deeper mechanistic understanding of the optical processes within nanocomposite thin films, absorptance (A) and diffuse transmission (T\diff) spectra have been acquired for I-BM and NS samples and are depicted in Figure 5 where A is defined as

\begin{equation}
A = 100 - T_{\text{tot}} - R_{\text{tot}}
\end{equation}

and

\begin{equation}
T_{\text{tot}} = T_{\text{spec}} + T_{\text{diff}}
\end{equation}

where T\tot is the total transmission and R\tot is the total reflection collected using an integrating-sphere-based spectrometer.

Absorptance of the films increases with higher loadings for both I-BM and NS samples but with very different spectral shapes. In the low-temperature phase, absorptance of I-BM is broad and featureless throughout the visible region of the electromagnetic spectrum before decreasing beyond 1500 nm, whereas in contrast, the NS sample has two defined absorption bands. The high-energy absorption is assigned to the $O 2p \rightarrow \pi^*$ interband transition, whereas the weaker low-energy absorption is assigned to the $d_{\parallel} \rightarrow \pi^*$ band gap transition, as described by Goodenough’s simplified model of the band structure of VO₂.67 In the high-temperature phase, when the band gap is closed, the absorption across the O 2p transition is still observed but a pronounced LSPR dominates the NIR region of the electromagnetic spectrum. For NS samples, the modulation in NIR absorptance between low- and high-temperature films is clearly centered at the inflection point between the two absorption bands. Such is not the case for I-BM samples.

Figure 5. Vis−NIR absorptance (A, B) and diffuse transmission (C, D) spectra for nanocomposite VO₂@SiO₂/MAA−EA nanocomposite films prepared from dispersions at nanocrystal loadings of 4 mg/10 mL (blue lines), 6 mg/10 mL (red lines), and 8 mg/10 mL VO₂ (green lines). In each case, the solid lines represent acquired at 35 °C, whereas dotted lines represent spectra acquired at 85 °C after equilibration for 10 min. (A, C) Sample I-BM and (B, D) sample NS. The inset in (D) magnifies the 300–750 nm region highlighting the systematic red-shift of the band maximum with VO₂ loading of the displayed spectra.
Interpretation of the absorbance spectra for NS samples is straightforward with the NIR modulation derived from the appearance of the LSPR absorption upon closing of the band gap. For I-BM samples, spectra for low-temperature films deviate between 600 and 1000 nm, absorbing broadly across the inflection point between O 2p π → π* interband and dπ → π* band gap transitions. We can conclude that in the low-temperature phase, significant internal light scattering within the film, arising from clustering of crystallites within larger agglomerates, facilitates a broad absorption in 600–1000 nm region. This broad absorption accounts for the NIR modulation onset beyond 1000 nm and further diminishes any LSPR-related ΔT_NIR.

We investigate light scattering profiles in the I-BM and NS samples further with diffuse transmission (Figure 5C,D). Interestingly, for both samples, the intensity of the scattering bands is not significantly different (<5%); however, clear differences are observed in the spectral line shapes and change in T_diff with temperature. For NS samples, which are homogeneous in terms of their dimensions and nature of encapsulation by a SiO2 shell, clear spectrally resolved bands appear in the visible region and are diminished in the NIR region of the electromagnetic spectrum (Figure 5D). In fact, the observed scattering bands are remarkably close to those theoretically predicted for homogeneous spherical particles. Scattering intensity in the low-temperature phase is greater and slightly red-shifted than that in the high-temperature phase; both attributes are explicable considering the differential in n between the MAA/EA copolymer host matrix and the M1 VO2 phase as compared with the R phase. T_diff measurements exhibit a clear red-shift of the scattering bands with increasing VO2@SiO2 loading concordant with predictions of size-dependent shifts (inset to Figure 5D). Since the crystallite size remains constant as a function of nanocrystal loading, the observed red-shift is attributed to an increasing “effective” particle size as a result of the agglomeration of nanocrystals to form larger particles within the MAA/EA matrix. In contrast, no discernible red-shift is observed for low-temperature I-BM samples; instead, the scattering is broader and less defined in the visible and extends well into the NIR. The magnitude of scattering between 600 and 1000 nm is in good agreement with the associated absorbance spectra (Figures 5A and 4C), signifying that the internal scattering is derived largely from the mismatch in the refractive index. Given the extensive agglomeration of I-BM VO2 particles during encapsulation with SiO2, multiple VO2 nanocrystals are likely incorporated in close proximity within a heterogeneous SiO2 shell. Such heterogeneous agglomeration likely accounts for the large gradient of n scattering in these samples and gives rise to the broad scattering signal.

Comparison of the absorbance and diffuse transmission spectra of the two samples highlights the significant impact that relatively subtle changes in disparate light scattering mechanisms (correlated directly or indirectly to size and size heterogeneity) can have on the optical performance of nanocomposite films. Consequently, mitigating the disparate light scattering mechanisms within these nanocomposite films requires not just control of particle size to avoid Mie scattering but also homogeneity of the refractive-index matching layer and individual dispersion of VO2@SiO2 nanocrystals within the host matrix. Figure 6 provides a visualization of the onset of NIR modulation, visible-light transmittance, and NIR modulation for the four nanocrystal dimensions at the same loading.

As discussed above, the NS samples have the smallest dimensions (44 ± 30 nm) and clearly show much greater visible-light transmittance as compared with the I, I-BM, and A samples as a result of a reduced scattering background. The NS samples with the smallest nanocrystal dimensions exhibit the best combination of high NIR modulation and visible-light transmittance (see also Table 1). The onset of NIR modulation at relatively shorter wavelengths implies the ability to dynamically adjust transmittance for a relatively greater region of the solar spectrum. For the three samples I, I-BM, and A, the onset of NIR modulation does not begin until further into the NIR, ca. 1660 nm for sample I, 1380 nm for sample A, and ca. 1150–1200 nm for I-BM. In contrast, for the NS samples, the onset of the drop is blue-shifted to ca. 740–750 nm, partly due to the appearance of LSPR band. Notably, NIR modulation below 700 nm is not desirable since that will bring about a pronounced change of the visible appearance of the film. Figure 6 thus clearly indicates the vastly greater visible-light transmittance and higher NIR modulation observed for the NS sample wherein light scattering is considerably mitigated as a result of the optimal nanocrystal dimensions, refractive-index matching, and dispersion. An NIR modulation of as much as 32.18% is accessible within these nanocomposite films, which results in a total dynamical modulation of transmitted light approaching 16.62%. The optical performance of our NS samples is indeed comparable to other recently reported values for VO2 composite films where considerable effort has been made to reduce light scattering. Zhang et al. and Miao et al. reduced Mie scattering by decreasing the as-synthesized VO2 particle size through grinding or ball-milling treatments and achieved a T_lum of 62.1% with ΔT_sol of 12.4% and a T_lum of 38.5% with

![Figure 6. Three-dimensional visualization of NIR modulation and visible-light transmittance plotted as a function of wavelength for the four sets of samples; I (purple spheres), A (blue squares), I-BM (black triangles), and NS (red diamonds). All samples shown here correspond to a concentration of 0.8 mg of VO2@SiO2/10 mL dispersion. The maximum visible transmittance is the maxima in the visible region from each 8 mg/10 mL 85 °C plot in Figure 4 and is constant for each plot (represented by an arrow across the maximum visible transmittance/wavelength plane).](image-url)
ΔT\text{vis} of 16.9%, respectively. Guo et al. have prepared ultrafine VO\textsubscript{2} nanoparticles using a unique one-step hydrothermal reaction in a self-released oxidizing atmosphere at relatively low temperatures and reported a T\text{lam} of 54.26% and a ΔT\textvis of 12.34%. As one of the best-in-class examples, Chen et al. have reported a 31.1% increase (from 38.9 to 51.0%) in T\text{lam} and an 11.0% increase (from 17.2 to 19.1%) in ΔT\textvis upon encapsulation of VO\textsubscript{2} nanospheres within a ZnO shell. Clear understanding and subsequent mitigation of light scattering mechanisms is of paramount importance to approach the limits of theoretically predicted performance.

To examine the dynamical behavior of the nanocomposite thin films, a time-dependent transmission experiment has been performed for nanocomposite thin films incorporating VO\textsubscript{2} NS and is shown in Figure 7. The temperature of the film has been ramped from room temperature to 73 °C, and spectra have been acquired from 1250 to 1430 nm as a function of time. The temperature values have been selected on the basis of the differential scanning calorimetry (DSC) trace shown in Figure S1. At each time interval, the temperature of the film is read using an internal temperature sensor, as shown in the inset to Figure 7. The transmission data shows that the transmission of the sample decreases drastically between 104 and 287 s (corresponding to film temperatures of 40 and 73 °C, respectively) and is constant thereafter. The maximum decrease in transmission at an elapsed time of 287 s is within 80% of the internal decrease in transmission at an elapsed time of 287 s is within 80% of the internal decrease in transmission at an elapsed time of 287 s is within 80% of the internal decrease in transmission.
and interstitial dopants will furthermore be utilized through modification of hydrothermal synthetic methods or post-synthetic modification to prepare nanocomposite thin films with transition temperatures designed to match the requirements of specific climate zones.29,60

**MATERIALS AND METHODS**

**Optical Simulations.** To simulate the light scattering properties of a single VO₂ nanowire, finite element analysis (FEA) was used. Scattering cross sections, absorption cross sections, and angular distributions of scattered light intensity were obtained on the basis of the FEA simulation. To evaluate the optical properties of nanowire composite films using the computed cross section and angular distribution, a conventional geometrical optics calculation (GO) was used. To simplify the calculation, the following assumptions were applied: (1) low fill factor of nanowires with no interactions between the nanowires, (2) nanowires aligned along the composite surface plane (which corresponds to the worst case for optical transmission), and (3) perpendicular incidence of light on the composite surface. A more comprehensive description of the simulation method and geometrical calculation has been published elsewhere.78

**Synthesis of VO₂ Nanowires.** VO₂ nanowires were synthesized through a variation of the one-step hydrothermal method reported in our previous work.26 The process from synthesis of VO₂ nanocrystals to casting of nanocomposite thin films is schematically outlined in Figure 3. Briefly, stoichiometric amounts of micron-sized V₂O₅ powder (Sigma-Aldrich, 98%) were placed in a poly(tetrafluoroethylene) receptacle with deionized water (ρ = 18.2 MΩ·cm, Barnstead Water Purification System) and a reducing agent (either 2-propanol or acetone). The cup was then sealed in an autoclave and heated at 210 °C for 18–72 h. The synthesized VO₂ (B) powder was then vacuum filtered and washed with 2-propanol, acetone, and/or water. The powders were subsequently annealed at 550 °C under inert Ar atmosphere for several hours to obtain phase-pure VO₂ nanocrystals crystallized in the M₁ phase upon cooling.47

**Milling of VO₂ Nanowires.** M₁ VO₂ nanowires synthesized hydrothermally via reduction with 2-propanol were dry-milled milled using methacrylate polymer beads. Samples were milled in 100 mg quantities for a total of 150 min at 30 min intervals using three polymer beads per tube in a SPEX SamplePrep 510 Mixer Mill.

**Synthesis of VO₂ NS.** VO₂ NS were synthesized via a two-step reaction based on the modification of a method reported in the literature.57–59 The first step involved the precipitation of VO(OH)₂ from the reaction of NH₄VO₃ and H₂NNH₂ at 80 °C in deionized water (ρ = 18.2 MΩ·cm, Barnstead Water Purification System). The VO(OH)₂ precipitate was then placed within a hydrothermal vessel and heated at 210 °C for 24–72 h. The product was finally isolated through centrifugation and used without further annealing or milling.

**Deposition of a SiO₂ Shell and Preparation of VO₂@SiO₂ Nanocrystals.** An amorphous silica shell was deposited onto nanocrystals using a modified Stöber method.85,59 Briefly, VO₂ nanocrystals (in quantities ranging from 24 to 240 mg) were ultrasonicated in a 4:1 (99.5% alcohol content, 100% nonenatured ethanol) ethanol/deionized water solution to obtain stable colloidal dispersions. For every 24 mg of VO₂ nanocrystals utilized, 400 μL of NH₄OH (0.25 M aqueous solution) was added as a catalyst followed by addition of 200 μL of tetraethylorthosilicate (yielding a final concentration of 0.02 M). The reaction was allowed to proceed for 25 min, and the VO₂@SiO₂ nanocrystals were collected by centrifugation. The solid collected via centrifugation was subsequently washed with copious amounts of 99.5% ethanol recovered by centrifugation. Three such cycles were performed prior to incorporation of the nanocrystals within the polymer matrices.

**Dispersion within Copolymer Matrix.** Polymer dispersion was carried out as reported in a previous work and is schematically outlined in Figure 3.59 VO₂@SiO₂ core–shell nanocrystals was dispersed in 10 mL of an alkaline aqueous solution (pH of ca. 11.3 prepared by addition of 2-amino-2-methyl-1-propanol containing 5% added water (Amresco) to deionized water) in a glass vial by ultrasonication. The dispersion was then gently stirred, and methacrylic acid/ethyl acrylate copolymer, Acrysol ASE-60 (Dow Chemical Company) was introduced at 1 wt % relative to water (adjusted to account for Acrysol ASE-60’s solid content being around 28 wt %). The solution was stirred more vigorously as the solution thickened to further homogeneously disperse the nanocrystals within the polymeric matrix. Upon dissolution of the methacrylic acid/ethyl acrylate copolymer in the alkaline solution (ca. 20 min), the dispersion was allowed to stand and used for casting thin films.

**Film Casting.** Films were cast from the polymer dispersions in a manner previously reported.59 Nanocomposite thin films of VO₂@SiO₂ were cast onto borosilicate glass substrates using 1.25 mL of the methacrylic acid/ethyl acrylate copolymer/VO₂ dispersion with various loadings of VO₂ nanocrystals (4–8 mg of VO₂@SiO₂ dispersed in 10 mL of the acrylate aqueous solution). The dispersion was placed on the glass slide and drawn down using a BYK film casting knife set to a wet thickness of 1 mm. The films were then allowed to dry overnight in an ambient environment. The dry thickness of the films was on the order of ca. 1–2 μm.

**Characterization.** High-resolution transmission electron microscopy (HR-TEM) images of VO₂ and VO₂@SiO₂ nanocrystals were obtained using a JEOL JEM-2010 instrument operated at 200 kV with a beam current of 100 mA, and SAED patterns were acquired using an FEI Tecnai G2 F20 ST field-emission TEM at a 200 kV operating voltage. Samples for HR-TEM were prepared by dispersing the VO₂ and VO₂ nanocrystals in 2-propanol or ethanol and dropping the dispersion onto 300 mesh copper grids coated with amorphous carbon. The grid was then allowed to dry under ambient conditions.

Differential scanning calorimetry (DSC) was performed using a Q2000 TA Instrument calorimeter with Al sample pans and lids. A scan rate of 10 °C/min was used in the temperature range between 0 and 100 °C.

Film thicknesses were determined using a Bruker Dimension Icon atomic force microscope operating in tapping mode. The AFM tip was a Mikromasch USA HQ:NSC35/Al BS three cantilever tapping mode n-type silicon tip with a radius of 8 nm, height of 12–18 μm, and a full tip cone angle of 40°. Powder X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance Eco X-ray powder diffractometer utilizing Cu Kα radiation (λ = 1.5418 Å).

Transmission spectra of nanocomposite films were obtained using a multilayer Bruker Vertex-70 Fourier transform infrared spectrometer utilizing a Pike Technologies temperature stage and allowed to equilibrate for 10 min at each
temperature. A PerkinElmer Lambda 950 UV/vis/NIR spectrophotometer with a 150 mm integrating sphere equipped with a custom designed and calibrated heating stage was also used for acquisition of transmission and absorbance spectra. Films were allowed to equilibrate for 5 min at each temperature. All transmission spectra were corrected for the transmission of the methacrylic acid/ethyl acrylate copolymer and glass by taking a blank spectra of glass and polymer and adding the reduction in optical transmittance attributed to the glass and copolymer alone; consequently, the measured values correspond to the optical properties of the embedded VO2 nanocrystals.

To standardize film performance, the solar (\(T_{sol}: 400–2500\) nm), luminous (\(T_{lum}: 400–780\) nm), and NIR (\(T_{NIR}: 780–2500\) nm) transmittance were determined according to the following equations:\(^{79–81}\)

\[
T_x = \frac{\phi_x(\lambda) T_x(\lambda) \, d\lambda}{\phi_x T_x(\lambda) \, d\lambda} \quad \text{where } x = \text{sol/lum/NIR} \tag{3}
\]

\[
\Delta T_x = T_x(\text{low temp}) - T_x(\text{high temp}) \tag{4}
\]

where \(T(\lambda)\) is the recorded film transmittance and \(\phi_x(\lambda)\) is the solar irradiance spectrum distribution for air mass 1.5 (corresponding to the sun at 37° above the horizon) over the wavelength range specified.\(^{11}\) The wavelength ranges for the sol, lum, and NIR ranges of the electromagnetic spectrum denoted as subscripts in eq 1 are defined as 400–2500, 400–780, and 780–2500 nm, respectively.

An iPhone 5s was acquired from Eigen Imaging Inc. and was used to image the transition in the NIR region of electromagnetic spectrum. Removal of the factory-installed 650 nm short-pass filter and utilization of an 850 nm long-pass filter acquired from Thorlabs Inc. allowed for exclusion of shorter wavelengths. The sensitivity range of the camera is between 850 and 1000 nm owing to the combination of long-pass filter and spectral response of the CMOS sensor of the camera. During the imaging experiment shown in Video S1, a 5 mg/10 mL loading NS nanocomposite VO2@SiO2/methacrylic acid/ethyl acrylate copolymer thin film was heated from 35 to 90 °C with a heat gun. Postprocessing of the video was done using Avidemux and Windows Movie Maker.

**ASSOCIATED CONTENT**

 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02093.

DSC traces, XRD patterns, and SAED patterns for four different size distributions of VO2 nanocrystals; digital photographs of aqueous dispersions of VO2@SiO2 nanocrystals dispersed in methacrylic acid/ethyl acrylate copolymer; digital photographs illustrating the visible-light transparency of nanocomposite VO2@SiO2 thin films (PDF).

The change in NIR transmittance of a NS nanocomposite VO2@SiO2 methacrylic acid/ethyl acrylate copolymer film is captured using a NIR-enabled camera (Video S1) (AVI).

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**Notes**

The authors declare no competing financial interest.

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