Title: Synthesis and Thermokinetic Analysis of Thermochromic VO_2 Particles for Smart Window Applications

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Abstract: Vanadium dioxide (VO_2) is often suggested as one of the most promising thermochromic materials for energy-efficient smart window applications due to its ability to undergo a reversible, structural phase transition (SPT) from monoclinic $VO_2(M)$ to tetragonal rutile $VO_2(R)$ at 68°C. This transition is accompanied by a distinct change in near-infrared (NIR) optical transmittance, enabling solar modulation without external power input. However, its practical implementation is hampered by complications such as high switching temperature, optical haze due to large particle size, and reduced functionality by doping and processing. In this work, we report on the scalable synthesis, processing, and thermokinetic characterization of undoped and W-doped VO_2 particles, targeting their application as thermochromic pigments for smart windows. [1,2]

Undoped and W-doped VO_2 powders were synthesized via reduction of V_2O_5 using oxalic acid in aqueous medium, followed by a controlled two-step calcination process. Undoped VO_2 exhibited a switching enthalpy close to the theoretical maximum ($55\,J\cdot g^{-1}$) and a narrow hysteresis. The introduction of W dopants in the VO_2 crystal lattice lowered the SPT temperature at an average rate of 23°C per at% of W. Doped VO2 particles containing 2 at% of W exhibited an SPT temperature of 21ºC while maintaining a high switching enthalpy of $37.5\ J\cdot g^{-1}$. The large initial particle size of 24 μm was successfully reduced by subsequent bead milling yielding sub-micron VO_2 particles of approximately 120 nm, though partial amorphization led to a 30-40% crystallinity loss, effectively halving the switching enthalpy.

Using the Friedman isoconversional method, the thermodynamic and kinetic profiles of the SPT were investigated as functions of particle size and doping percentage. The activation energy for the phase transition of $VO_2(M)$ to $VO_2(R)$ decreased from 1610 to 381 $kJ\cdot mol^{-1}$ upon bead milling, correlating with a loss in enthalpy. This processing step also introduced a kinetic asymmetry in the reversible phase transition, where the transition of $VO_2(R)$ to $VO_2(M)$ demonstrates a lower activation energy compared to the opposite transition. W-doping introduced additional structural defects, further modulating switching kinetics. Below 2 at-% W, transitions remained quasi-symmetric. Above this threshold asymmetry emerged, with this time a lower activation energy for the transition of $VO_2(M)$ to $VO_2(R)$. These observations

illustrate that the defects induced by bead milling or by W-doping display a different effect on the SPT.

The milled VO_2 particles were mixed into PVB to make laminates of two glass plates with the nanocomposite thermochromic film as interlayer. The optimal laminates exhibited a luminous transmittance of 54.7% and a solar modulation of 9.4%. Moderate visible light scattering was attributed to the presence of particles exceeding 100 nm in size. A comparison of the switching kinetics between the VO_2 powders and the nanocomposite laminates revealed comparable phase transition rates.

These results illustrate that precise control over VO_2 particle size, crystallinity, and defect structure is critical for optimizing thermochromic performance in smart window applications. The successful integration of VO_2 particles into composite films demonstrates their potential for energy-efficient glazing solutions reducing energy consumption in buildings.

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[1] L. Calvi et al. "A comparative study on the switching kinetics of W/VO2 powders and VO2 coatings and their implications for thermochromic glazing" Solar Energy Materials and Solar Cells (2021) 110977
[2] L. Calvi et al. "Thermochromic glass laminates comprising W/VO2 nanoparticles obtained by wet bead milling: An in-depth study of the switching performance" Solar Energy Materials and Solar Cells (2023) 112350