Continuous Flow Synthesis of Spin Crossover Materials for Solid-State Green Refrigeration

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The increasing global demand for cooling technologies represents a major environmental challenge. Recent reports indicate that refrigeration systems account for up to 20% of global electricity consumption and approximately 7.5% of total CO_2 emissions, arising from both energy use and refrigerant leakage [1]. In this context, the development of alternative solid-state cooling technologies is crucial to reduce the environmental impact of current vapor-compression systems. Among emerging solutions, barocaloric cooling based on mechanocaloric effects [2] has attracted significant attention. Spin-crossover (SCO) materials [3], in particular, exhibit large and reversible entropy changes associated with electronic transitions under external stimuli such as temperature or pressure. Their strong coupling between structural, electronic, and thermodynamic properties, combined with sensitivity to relatively low pressures, makes them promising candidates for next-generation cooling devices [4].

However, a major limitation for their technological implementation lies in their synthesis, processing and scaling up. SCO materials are typically obtained as poorly controlled polycrystalline powders through batch precipitation, leading to limited reproducibility, broad particle size distributions, and strong sensitivity to synthesis conditions. Since their functional properties are directly linked to microstructure, morphology, and phase identity, controlling nucleation and growth mechanisms is essential [5].

In this work, continuous flow chemistry is explored as a powerful strategy to overcome these limitations. Flow processes enable precise control over reaction parameters such as mixing, residence time, concentration, and temperature, allowing the decoupling of nucleation and growth steps [6]. This control directly impacts particle size and crystallinity, highlighting the importance of mixing regimes and concentration in determining final material properties. In particular, the implementation of quench strategies enables the limitation of particle growth by rapidly modifying reaction conditions, leading to smaller and more controlled particles [7].

In parallel, the integration of supercritical CO_2 ($scCO_2$) processing is investigated as a unique transport and extraction properties, enabling efficient solvent removal without capillary stresses and preserving particle morphology and microstructure [8]. The combination of continuous flow synthesis with $scCO_2$ drying (with or without co-solvents) provides a promising route toward controlled, reproducible, and scalable production of SCO molecular materials [7]. However, the implementation of such an approach for molecular coordination materials is far from trivial, as it involves fast precipitation reactions, strong sensitivity to mixing conditions, and complex nucleation–growth mechanisms that critically influence phase formation and final properties. The ultimate objective of this work is to develop an integrated and sustainable process enabling the large-scale production of spin-crossover materials for their integration into barocaloric heat exchangers, contributing to the emergence of alternative refrigeration technologies.

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