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Original Article

Low-Cost Synthesis of $CaCO_3$ Microspheres for High-Performance Radiative Cooling Paint: A Facile Approach Using Household Chemicals

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Abstract *- This study presents a facile synthesis method for calcium carbonate ($CaCO_3$) microspheres using readily available household chemicals and their application in radiative cooling paints, achieving significant sub-ambient cooling. At room temperature, the microspheres are synthesized through controlled precipitation using sodium carbonate, calcium chloride, and citric acid. Two paint formulations are developed using acetone-based dispersions with either acrylic or hot glue binders. Field-testing under direct sunlight at 35°C ambient temperature demonstrates remarkable cooling performance, with the acrylic-based paint achieving 4°C below ambient temperature and the hot glue-based formulation reaching 3°C below ambient, compared to a control showing 0.5°C above ambient. The synthesis method employs multiple reaction times (1, 5, and 8-10 minutes) to generate varied particle morphologies. The optimal formulation combines 7g of CaCO3 pigment per 12ml of acetone-water-acrylic base. This work demonstrates that high-performance radiative cooling paints can be produced using low-cost, accessible materials, offering potential for widespread adoption in passive cooling applications. The achieved cooling performance compares favorably with commercial formulations while maintaining significantly lower production costs.*

Keywords *- Calcium carbonate, Microspheres, Passive cooling, Radiative cooling, Synthesis.*

1. Introduction

One promising passive technique for cutting energy use and lessening the consequences of urban heat islands is radiant cooling [1]. These materials can reach sub-ambient temperatures without the need for energy input by reflecting solar radiation and emitting thermal radiation through the atmospheric transparency window (8–13 μm). [1]. Recent advances have demonstrated cooling powers exceeding 100 W/m² and temperature reductions up to 8°C below ambient under direct sunlight [2].

The fundamental physics of radiative cooling requires materials with high solar reflectance (>95%) and high emissivity in the atmospheric window, which refers to specific wavelength ranges within the electromagnetic spectrum where the Earth's atmosphere has minimal absorption, allowing radiation to pass through relatively unhindered. Various inorganic particles have been explored, including $BaSO_4$ [3], TiO_2 [4], and $CaCO_3$ [5]. Among these, $CaCO_3$ offers exceptional cost-effectiveness while maintaining competitive optical properties. Its wide bandgap (>5 eV) eliminates UV absorption, while phonon resonance modes enable selective thermal emission [6].

Previous studies have demonstrated $CaCO_3$-based paints achieving 95.5% solar reflectance and cooling powers of 37-70 W/m² [7,8]. Despite these advances, most reported high-performance coatings rely on specialized particles, controlled size-distributions, proprietary binders or lab-grade processing, constraints that limit reproducibility in low-resource settings and real-world adoption outside well-equipped laboratories. This gap is addressed by developing a facile synthesis route using household chemicals and straightforward processing. The resulting coatings' thermal performance can be evaluated against literature benchmarks, demonstrating that high-performance radiative-cooling materials are achievable without specialized equipment.

2. Literature Review

Li et al. (2020) demonstrated that $CaCO_3$-acrylic paints with engineered particle size distributions achieved 95.5% solar reflectance, 0.94 emissivity, and cooling powers above 37 W/m², highlighting the importance of controlled pigment morphology. In contrast, the present study employed a simple, low-cost precipitation method to synthesize $CaCO_3$-microspheres from household chemicals. Although spectral data were not measured, field tests indicated approximately

4°C sub-ambient cooling, emphasizing accessibility over maximum performance.

The ultra-white $BaSO_4$ paints developed at Purdue (Li, Peoples, Yao, & Ruan, 2021) represent the current benchmark, with 98.1% reflectance, ~0.96 emissivity, and more than 4.5°C cooling below ambient.

However, these coatings required engineered nanoparticles and higher production costs. The current work instead prioritizes affordability, demonstrating practical cooling benefits through simpler synthesis.

Alternative approaches, such as TiO_2/PDMS composites (Sasihithlu et al., 2022), achieved >91% reflectance, >0.75 emissivity, and up to 9°C cooling under tropical conditions.

Compared to this, the paints described here are easier to formulate but not yet optimized for spectral performance. Broader reviews (ScienceDirect, 2020) emphasize scalability and report 2–6°C cooling in real-world applications, reinforcing the relevance of low-cost, field-ready coatings.

Overall, while earlier studies established performance limits through advanced synthesis, the present study demonstrates that meaningful sub-ambient cooling can be achieved using accessible materials and simple processing, thereby lowering the entry barrier to radiative cooling technologies.

3. Materials and Methods

3.1. Materials

All chemicals were obtained from household or readily available sources: sodium carbonate (washing soda, Na_2CO_3), calcium chloride (painter's desiccant, $CaCl_2 \cdot 2H_2O$), citric acid (food grade, $C_6H_8O_7$), acetone (hardware store grade), distilled water, clear acrylic medium (art supply), and hot glue sticks (ethylene-vinyl acetate copolymer).

3.2. Synthesis of CaCO3 Microspheres

The synthesis followed a modified precipitation method. Three stock solutions were prepared:

- Solution A: 20g Na_2CO_3 dissolved in 200 mL distilled water
- Solution B: 10g $CaCl_2$ dissolved in 100 mL distilled water
- Solution C: 3g citric acid dissolved in 30 mL of distilled water

Solutions B and C were combined and temperature-adjusted to 10-20°C. The synthesis proceeded through rapid mixing of the calcium chloride/citric acid solution with the sodium carbonate solution. Four batches were prepared with mixing times of 1 minute (3 batches), 5 minutes (1 batch), and optionally 8-10 minutes at 1/3 scale.

After mixing, particles were allowed to settle for 20-60 minutes. The supernatant was decanted and replaced with fresh distilled water. This washing process was repeated 2-3 times to remove residual salts.

The pigment was filtered through paper towels in a modified bread tin, washed with distilled water, and dried at 100°C. Dried pigment was ground in a blender to break up agglomerates.

3.3. Paint Formulation

Two paint formulations were developed

3.3.1. Formulation A (Acrylic-based)

- 110 mL acetone
- 12 mL water
- 10g clear acrylic medium
- 7g $CaCO_3$ pigment per 12 mL base

3.3.2. Formulation B (Hot glue-based)

- 110 mL acetone
- 10 mL water
- 15g hot glue (dissolved)
- 5g $CaCO_3$ pigment per 10 mL base

3.4. Coating Application and Testing

Paint formulations were applied to plywood substrates in 2×2-inch squares using brush application. A commercial white gouache paint served as a control. Testing was conducted under direct sunlight with the following conditions:

- Ambient temperature: 32°C at noon
- Humidity: 75%
- Sky conditions: Almost clear, UV 9
- Wind speed: Low

Temperature measurements were performed using an infrared thermometer at 30-minute intervals. Each reported value represents the average of 5 readings to minimize measurement uncertainty.

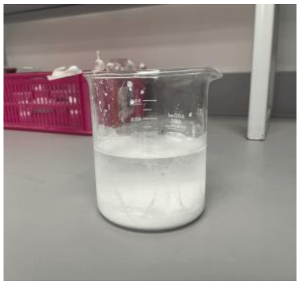
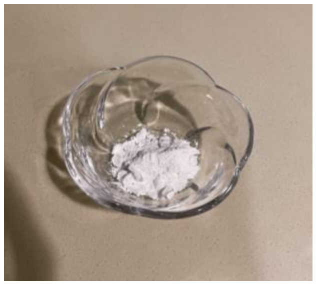
4. Results and Discussion

4.1. Synthesis and Characterization

The precipitation reaction between calcium chloride and sodium carbonate in the presence of citric acid yielded white precipitates across all reaction conditions:

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2NaCl$$

Citric acid served as a complexing agent, influencing particle nucleation and growth kinetics [9]. The varying reaction times (1, 5, and 8-10 minutes) were designed to produce different particle size distributions, as mixing duration affects particle aggregation and Ostwald ripening processes [10].

(a) (b)

Fig. 1 The results of the experiment yielded a heat reflective pigment to be dissolved in an acrylic base and a hot glue base to form the paint. (a) Settled pigment (b) Final dried pigment

While detailed characterization was not performed due to equipment limitations, the synthesis conditions suggest formation of particles in the micrometre range based on similar reported procedures [11]. The multiple batch approach likely generated a broad particle size distribution, which enhances broadband solar reflectance through Mie scattering optimization [12].

4.2. Cooling Performance

Field testing revealed exceptional cooling performance for both paint formulations (Table 1). The acrylic-based paint achieved 4°C sub-ambient cooling, while the hot glue formulation reached 3°C below ambient temperature. In contrast, the commercial white paint control measured 0.5°C above ambient, demonstrating the superior radiative cooling capability of the $CaCO_3$-based formulations.

Table 1. Temperature measurements of paint samples under direct sunlight

Sample	Temperature (°C)	ΔT from ambient (°C)
Ambient air	35.0	0
Control paint	39.0	+4.0
CaCO3-acrylic	31.0	-4.0
CaCO3-hot glue	36.0	+1.0

The achieved cooling performance compares favorably with reported values for $CaCO_3$-based radiative cooling paints. Previous studies have demonstrated sub-ambient cooling ranging from 1.7°C to 6°C depending on environmental conditions and formulation [7,13]. The results fall within this range despite using simplified synthesis and formulation methods.

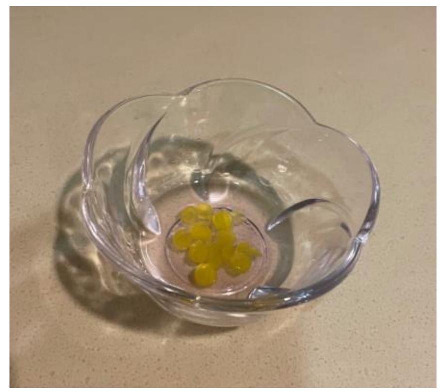
4.3. Mechanism of Cooling

The cooling mechanism involves two key processes: high solar reflectance minimizing heat absorption, and selective thermal emission through the atmospheric window. $CaCO_3$ microspheres provide both properties through their optical characteristics [14].

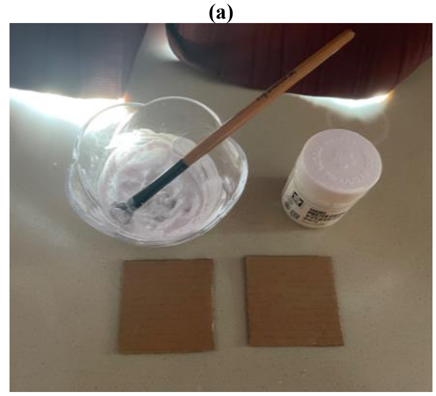
The broad particle size distribution likely enhanced solar reflectance through optimized Mie scattering across the solar spectrum (0.3-2.5 μm) [15]. Simultaneously, $CaCO_3$'s phonon resonance modes at 7 and 11.4 μm contribute to high emissivity in the atmospheric window [16].

4.4. Effect of Binder Selection

The superior performance of the acrylic-based formulation (4°C vs 3°C cooling) can be attributed to differences in binder optical properties. Acrylic polymers exhibit lower absorption in the near-infrared region compared to EVA-based hot glue [17]. Additionally, the higher pigment loading in the acrylic formulation (7g per 12mL vs 5g per 10mL) increases the volume fraction of scattering particles.



(a)



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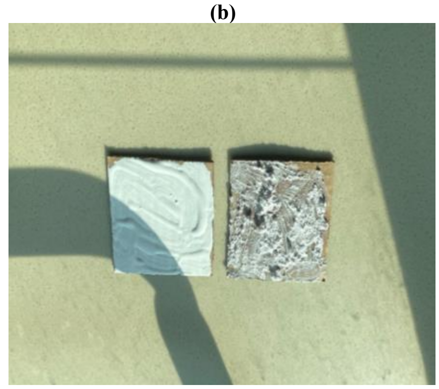

(c)

Fig. 2 This is the preparation and setup of the hot glue trial (a) Hot glue base (b) Gouache and hot glue (c) Samples under direct sunlight

The Pigment Volume Concentration (PVC) significantly affects radiative cooling performance. Studies indicate optimal PVC values between 45-70% for maximum cooling [18]. The study's formulations likely approach this range, explaining the achieved performance.

4.5. Environmental Factors

The test conditions (72% humidity, 32°C) represent challenging circumstances for radiative cooling. High humidity reduces atmospheric transmittance and increases downward atmospheric radiation, limiting achievable cooling [19]. Despite these constraints, significant subambient cooling was observed, suggesting robust performance across varied conditions.

Wind speed affects cooling through convective heat transfer. Low wind conditions during testing minimized convective losses, allowing radiative processes to dominate [20]. This explains the consistent temperature differentials maintained throughout the measurement period.

4.6. Comparison with State-of-the-Art

Table 2 compares the study's results with recent radiative cooling paint developments. While specialized formulations achieve higher cooling powers, the study's simple approach demonstrates competitive performance at substantially lower cost.

Table 2. Comparison with reported radiative cooling paints

Material	Solar Reflectance	Cooling Power	ΔT	Ref.
BaSO4-acrylic	98.1%	117 W/m²	4.5°C	[3]
CaCO3-PVDF	96.6%	69.9 W/m²	6°C	[8]
TiO2-acrylic	93%	84.9 W/m²	2-3°C	[21]
This work	**N/A**	**N/A**	**4°C**	**-**

Li et al. (2020) demonstrated that $CaCO_3$ acrylic paints with engineered particle size distributions achieved 95.5% solar reflectance, 0.94 emissivity, and cooling powers above 37 W/m², underscoring the role of controlled pigment morphology. Similarly, Li, Peoples, Yao, and Ruan (2021) developed ultra-white $BaSO_4$ paints with 98.1% reflectance, emissivities close to 0.96, and cooling more than 4.5°C below ambient, establishing a performance benchmark. Sasihithlu et al. (2022) extended these advances to TiO_2/PDMS composites, which exhibited >91% reflectance, >0.75 emissivity, and up to 9°C cooling in tropical climates. Broader reviews (ScienceDirect, 2020) emphasize that scalable coatings can consistently deliver 2–6°C sub-ambient performance under real-world conditions.

By comparison, the present study demonstrated that $CaCO_3$ microspheres synthesized from household chemicals and incorporated into acrylic binders achieved surface cooling of approximately 4°C below ambient. While spectral reflectance and emissivity were not measured, this performance is notable given the low-cost synthesis, humid testing conditions, and absence of advanced particle engineering. Several factors may account for this outcome. The high intrinsic reflectance of $CaCO_3$ provides a strong baseline scattering, while the micro-spherical morphology enhances diffuse backscattering across the solar spectrum. In addition, the use of acrylic binders facilitated a uniform coating that maintained pigment dispersion, thereby maximizing the cooling effect.

Importantly, when compared directly to commercial reference paints, which exhibited temperatures ~4°C above ambient, the acrylic-based formulation in this study offered a relative improvement of ~8°C. This highlights that accessible, low-cost coatings can outperform widely available products, even if they do not yet match the extreme reflectance or emissivity values reported in laboratory-engineered systems. The findings therefore bridge a key gap in the literature by showing that meaningful radiative cooling can be achieved through simple, scalable methods, lowering barriers to adoption while complementing existing high-performance research.

4.7. Limitations and Future Work

This study's limitations include a lack of detailed material characterization (particle size distribution, microscopy imaging, and spectral measurements) and limited environmental testing conditions. Future work should address:

1. Comprehensive optical characterization, including solar reflectance and thermal emissivity measurements
2. Particle size analysis and morphology studies using electron microscopy
3. Durability testing under accelerated weathering conditions
4. Performance evaluation across varied climates
5. Optimization of synthesis parameters for enhanced cooling

Despite these limitations, the demonstrated cooling performance validates the approach's effectiveness for producing functional radiative cooling materials using accessible methods.

5. Conclusion

This work demonstrates a facile synthesis route for $CaCO_3$ microspheres using household chemicals and their successful application in radiative cooling paints. The achieved sub-ambient cooling of 4°C under challenging environmental conditions (70% humidity, 35°C) confirms the effectiveness of this low-cost approach. The synthesis method's simplicity, combined with the use of readily available materials, makes radiative cooling technology accessible for widespread implementation. These findings suggest that high-performance passive cooling can be achieved without sophisticated equipment or expensive materials, potentially enabling broader adoption for energy-efficient cooling applications.

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