



Well-ordered nanoporous materials for low-temperature water phase changes and solar evaporative cooling



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ABSTRACT

The interaction of solar radiation with nanoporous composites with a high water vapor adsorption capacity compared to materials used in external building surfaces was investigated in a wind tunnel with adjustable environmental parameters. Prior to the tunnel experiments, all of the materials were characterized using irriavious techniques, and their thermal and optical properties were determined. In cyclic experiments inside the tunnel, the maximum temperature in the nanoporous materials under simulated solar radiation was considerably lower than the corresponding temperature inside marble dust or soil. In addition, the temperature differences between the humid and non-humid nanoporous samples under simultaneous irradiation increased with increasing solar absorbance, which was primarily due to evaporative cooling. In addition, solar reflectance and emittance increased upon water vapor adsorption. Energy balance analysis revealed that the absorbed solar radiation was primarily transformed to heat desorption energy to compensate for the electrostatic attraction of water vapor to the negatively charged particle surfaces. A decrease in the released heat in the environment indicates the need for more sun- and hydrophilic urban surfaces.

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1. Introduction

Among the most frequently noted effects of climatic change is the urban heat island phenomenon (UHI). Even small cities, such as Agrinio, Greece, can be as much as 5 °C warmer than their surrounding rural areas [1]. The effect results in an increase in cooling energy demand of buildings, deterioration of different environmental parameters, release of pollutants to the atmosphere, degradation of construction materials and reduction of thermal comfort or even an increase in the number of deaths. In addition, conventional air conditioning is currently the major technology to compensate for the increased indoor temperatures during the summer. Conventional air conditioning is the major contributor to peak electricity demand in hot climate countries or during the summer (e.g., accounts for as much as 40 percent of the peak demand in Shanghai [2], which can increase to 100% due to the UHI effect [3]). Therefore, the reduction in the use of mechanical (active) systems and the development of alternative, sustainable and efficient cooling technologies are vital.

Due to the significance of the urban heat island problem and the increased energy consumption of buildings, there has been additional focus on developing appropriate methods for passive

cooling of buildings. Therefore, some traditional passive cooling methods, such as green and water spaces as well as “cool” materials in the urban environment, have been studied and being re-developed in a more eco-efficient manner. The basic principle of these methods involves the restriction and/or the removal of heat from the building environment primarily using physical processes consisting of radiation reflection or re-emission, convection and phase changes, such as simple evaporation followed by transpiration or desorption. The first two processes transfer the heat to the ambient atmosphere, and the third process transforms it into different states of matter. In this context, the most well developed cooling technologies for reducing the heating loads are cool and green surfaces [4]. Both technologies can lower the surface temperatures to decrease the corresponding heat flux to the atmosphere. The solar albedo and hydrological performance associated with the released latent heat are the key variables that determine the effectiveness of cool and green surfaces, respectively [4–6]. However, the practical applicability of these methods highly depends on the local climate, and there are important considerations for both technologies. For example, the reflectance of cool coatings is reduced by as much as 15% during the first year of application due to weathering [7,8]. In addition, high reflectance coatings are appropriate for the hot Mediterranean climate but the reflectivity should be optimized to 0.6–0.7 for colder climates to account for winter losses [9]. The effectiveness of the high albedo to mitigate high urban temperatures during the night is limited

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[10]. Green spaces could produce the same effect as cool materials if they continuously use water resources for irrigation and are regularly irrigated and planted with a dense mix of actively transpiring vegetation. Although the cost of green spaces, such as roofs, has been greatly reduced, the water required for irrigation and drainage systems, the required intensive maintenance and the dependence on the local climate conditions can limit their worldwide applicability. Recently, Raman et al. [11] reported that the use of an integrated photonic solar reflector and thermal emitter consisting of seven layers of HfO_2 and SiO_2 reflected 97% of incident sunlight while emitting strongly and selectively in the atmospheric transparency window. Surface temperatures of nearly 5 °C below the ambient air temperature were observed under direct sunlight due to this radiative cooling. However, this complex surface is highly sunphobic and not consistent with natural processes, such as evapotranspiration, that govern our life. Therefore, new and more efficient materials and procedures are needed [4].

In the last few years, there has been extensive research on the use of porous materials and lotus ceramics for evaporative cooling of building components or pavement of outdoor spaces [2,12–14]. According to this method, the retained water in the material pores, which are primarily created from packed beds, is evaporated, and the material temperature is reduced due to the release of latent heat. The effect is much faster than that of bulk water due to the increased surface area provided by the pores. In turn, the heat flux in the building is reduced due to the reduction of material temperatures. The principle has been validated with the addition of liquid water in natural porous materials [2], synthetic and aluminum pillared clays [15], modified lignite fly ash [16] and organic polymers [17]. Recently, the principle was applied to moisture sorption on highly hydrophilic natural sepiolite without the addition of liquid water [18]. With moisture adsorption during the night on multiporous sepiolite at 70% relative humidity (RH) (to resemble the outdoor conditions at night), lower surface temperatures were observed under irradiation compared to concrete due to heat absorption for water evaporation and desorption with the accompanied mass reduction [18]. However, the intensity of the applied radiation in these experiments was low. Therefore, the cooling process through atmospheric water vapor adsorption at the building–environment interface needs to be validated by solar simulated radiation. Therefore, tailored porous materials with a high water vapor capacity should be studied. In addition, the temperature of water vapor desorption, which depends on the porous structure, should be selected to match outdoor conditions.

In this study, we optimized the selection and preparation of the porous host using the Kelvin equation, and we validated the optimization via solar-heat transformation experiments. The materials were prepared from tetraethylorthosilicate (TEOS) silica source and characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), thermogravimetry (TG), UV/vis/NIR spectrophotometry and water vapor adsorption isotherms. The temperature differences of the humid and non-humid samples, which were irradiated individually or simultaneously in a two compartment holder, were determined at different sample reflectances in a wind tunnel with controllable environmental conditions.

2. Nanoporosity optimization for solar evaporative cooling

When water is confined in pores with a small diameter (with dimensions of some water molecules), it exhibits a broad range of properties. Due to pore confinement and the appearance of liquid (vapor)–wall and liquid (vapor)–liquid (vapor) forces, the observed shifts in transitions and reduction in the critical points of the phase changes are different from that of the typical free water [19].

Therefore, we can distinguish between water vapor adsorption in the nanopores with widths of less than 2 nm and that in 2–50 nm nanopores. In smaller nanopores, pore and cooperative filling is the primary driving mechanism for adsorption. This robust interaction can be higher than the intermolecular dispersion forces that lead to condensation of vapor, and confined water is less prone to typical condensation than free fluid [20]. Therefore, temperatures higher than 95 °C are used for water vapor desorption from strong hydrophilic porous materials, such as zeolites, aluminophosphates and metal organic frameworks (MOFs), which are being studied for heat storage and pumps [21]. In the materials with 2–50 nm nanopores, capillary condensation, which is an exothermic process, was observed (after molecular layering on the pore walls) with the presence of a dense liquid-like state in porous sorbents that have a chemical potential lower than its bulk saturation value [22]. In cylindrical pores, such as the pores in Mobil crystalline materials (MCM-41), the adsorbent is confined in two dimensions, and the confinement effects are stronger with capillary condensation being observed at lower pressures. A similar effect occurs on desorption with the system persisting in the liquid state at pressures below the true equilibrium value. This metastability is similar to that observed in bulk liquids in the gas–liquid coexistence region but more pronounced in confined systems. In a nanoporous solid with a low silane concentration and hydrophobicity, the condensed water is expected to desorb at much lower temperatures than free water. Therefore, the principle of solar cooling with nanoporous materials can be extended to account for all of the phase changes within the adsorption–condensation–evaporation–desorption cycle (Fig. 1). After overnight water vapor adsorption and capillary condensation, liquid water in the nanopores will be desorbed at lower temperatures than bulk liquids due to solar radiation absorption that provides sensible and latent heats as well as the heat of desorption. Analogous to water vapor desorption from leaves through evapotranspiration, porous solids can also use heat from their surroundings and longwave anthropogenic radiation to evaporate sorbed water. Subsequently, the void space in the hydrophilic porous material will act as an insulator after water vapor desorption to transform the low hydrophilic material at high nighttime humidity to a hydrophobic material at low daytime RH. In this way, the temperature of the nanoporous material surface is expected to decrease after these low-temperature solar-heat transformations.

The solar cooling effect of the nanoporous material can be maximized by optimizing the pore diameter of the material according to the outdoor environmental conditions (i.e., temperature and RH). In hot and humid (like Japan) or dry climates (i.e., Mediterranean), RH exceeds 50% during the night, and the outdoor material temperature can be as much as 50 °C due to solar radiation. Therefore, moisture sorption–desorption for evaporative cooling applications is a suitable approach in high humidity warmer climates where the RH allows for recharging at night. The curvature radius (ρ) for capillary condensation and evaporation within the pores at a relative pressure P/P_0 is defined by the Kelvin equation [23]

$$\rho = \frac{-2\gamma Vm}{RT \ln\left(\frac{P}{P_0}\right)} \quad (1)$$

where Vm is the molar volume and γ is the interfacial tension of the adsorbate in the bulk liquid condition. The radius of curvature for a cylindrical pore is the ratio of the pore radius to the cosine of the contact angle of water (with values close to 1 for hydrophilic porous materials to complete wetting) at the liquid–solid interface. The molar volume (Vm) is assumed to be $1.8 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$, and the interfacial tension (γ) is given as a function of isothermal temperature (T) by the Vargaftik interpolating

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