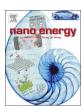


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Full paper

Hybrid plasmonic nanoresonators as efficient solar heat shields



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ABSTRACT

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A solar heat shield coating featuring the combination of plasmonic nanostructures in silica-based insulating materials has been developed and tested under conditions resembling natural sunlight exposure. Our results when implementing this coating on standard glazing reveal a blocking efficiency higher than 40%, compatible with a notable preservation of visible light transmittance above 75%. This strategy is (i) cost-effective, as only requires minute amounts of absorbent material in order to obtain the desired effect; (ii) straightforward, because no particular ordering of the plasmon resonators is needed onto the glass substrate; (iii) eco-friendly, as no metal leaching is observed once the gold is encapsulated; and (iv) retrofit-capable, given the fact that these nanostructures can be easily incorporated onto pre-installed glazing. All of these features emphasize the great potential of this approach in the search of more sustainable technologies for the fenestration industry.

1. Introduction

In most developed countries buildings account for at least 40% of the total energy consumption, the production of which is responsible for more than one third of the global greenhouse gas (GHG) emissions [1,2]. In particular, thermal losses and excessive solar irradiation through glass windows amount to 60% of the total expenditure in air conditioned and heating systems [3]. For this reason, a great deal of work has been devoted in recent years to the development of thermallyefficient glazing materials [4]. Tinted glazing is one of the most widely used technologies in sustainable windows [5] to absorb a large fraction of the incoming solar radiation, thus reducing the solar heat gain (SHG) and glare, as well as visible light transmittance (VLT). Unfortunately, traditional tinted glazing presents a greater reduction in VLT than SHG, which ultimately leads to an undesired reduction of daylighting in indoor areas. The necessary compromise between these essential but incompatible features limits the applicability of the tinting approach, because the achieved reduction in the demand of cooling energy may be offset by the need of additional electrical lighting. Additionally, reflective coatings applied to either clear or tinted glazing have been used to obtain larger reduction in SHG by increasing the surface reflectivity. However, this strategy blocks visible light more than heat, thus leading again to an undesired reduction of VLT.

In this context, it is important to take into account the impact that windows with reflective treatments may have on the outside. These types of materials act as mirrors that can produce blinding glare in adjacent buildings and eventually in nearby traffic [6]. Furthermore, an intensification of solar radiation on neighboring constructions can take place, hence contributing to the urban heat island (UHI) effect [7,8].

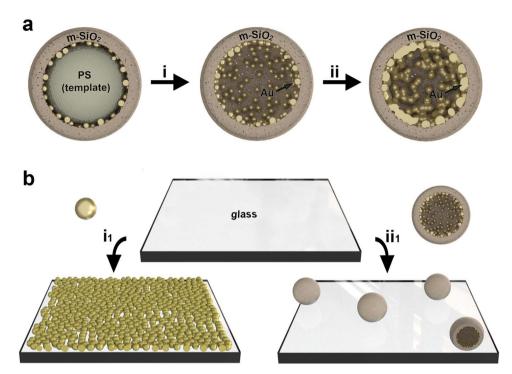
Spectrally selective coatings have emerged as an interesting alternative to purely reflective materials. This is the case of low-emissivity (low-e) glazing, which allows the transmission of visible light while blocking (reflecting) longer wavelengths (mostly NIR) responsible for unwanted heat generation. Nevertheless, low-e coatings still exhibit high reflection that can produce an increase in the UHI effect.

Selective solar absorption has also become an important technological approach for combining heating and daylighting, as well as for cooling through radiative heat transfer to outer space [9]. In this regard, special consideration has been given to the implementation of micro- and nanostructured coatings, as they offer a high degree of

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Scheme 1. Fabrication of hybrid materials for solar-efficient glazing. (a) Removal of sacrificial polystyrene (PS) template to yield a void@AuNP@silica nanocapsule (i), and autocatalytic growth of metallic Au by means of a pre-reduced Au^+ solution (ii). (b) Deposition of successive layers of colloidal Au nanoparticles (i₁) and plasmonic nanocapsules (ii₁) onto the surface of a glass slide.

control over the absorbing capabilities of the surfaces [10]. Among the wide variety of selective electromagnetic absorbers, plasmonic structures occupy a prominent place [11]. This is largely due to the versatility of available synthesis methods used to produce these materials, which allows fine tuning of their absorbance features in order to meet the requirements for the desired application. This flexibility has fueled the use of plasmonic nanostructures in areas such as selective thermal emission [12,13], biosensing [14–16], solar energy harvesting [17,18], structural coloring [19,20], and photodetection [21,22]. However, despite the extensive literature on the optical properties of plasmonic materials [23,24], no much attention has been devoted to their application as solar heat shields for the implementation of energy-efficient glazing under natural sunlight exposure conditions.

In a different approach, highly porous silica aerogels have also shown great promise as insulating materials in the fenestration industry, because they combine high transparency and low thermal conductivity [25]. Nevertheless, the resulting structures are extremely sensitive to moisture and they present low tensile strength [26], so that they need to be supplemented with waterproof components in sandwiched architectures that substantially increase the cost of the final glazing.

As a viable alternative to the approaches discussed above, here we focus on the great potential of hybrid materials formed by light-absorbing plasmonic nanostructures and highly porous silica-based insulating elements for controlling the passage of solar radiation through glazing. Specifically, we report on the controlled growth of gold nanoparticles (AuNPs) on the inner walls of mesoporous silica capsules and the subsequent deposition of the resulting nanocomposites on a single-pane regular glass (Scheme 1). Through this approach,

we achieve an efficient reduction of SHG, while preserving VLT. Besides its simplicity, this strategy has the following appealing properties: (i) cost-effectiveness, because it only requires minute amounts of absorbent material in order to obtain the desired effect; (ii) ecofriendliness, as no metal leaching is observed once the gold particles are encapsulated; and (iii) retrofit capabilities, since these nanostructures can be easily incorporated onto preinstalled glazing.

Colloidal gold nanoparticles can strongly absorb visible light at spectral regions overlapping with their collective conduction-electron oscillations known as surface-plasmon resonances (SPRs) [27]. Additionally, when AuNPs are assembled into close-packed arrays, each individual particle can couple with its neighboring particles via near-field plasmonic interaction, thus giving rise to hybridized plasmon-resonance modes that are delocalized over the entire nanostructure [28]. As a result of this coupling, the SPR bands broaden and redshift to the near-infrared (NIR) spectral region (~780–2500 nm). Considering that the NIR accounts for 52% of the sun irradiance power, it is natural to exploit the optical response of arrayed AuNPs to capture an important fraction of the sunlight power, while preserving VLT. In this direction, we note the critical role that mesoporous silica may play as an optical element beyond being a simple encapsulating material.

In a complementary direction, hollow silica nanoshells exhibit remarkable insulating properties accompanied by a high optical transparency [29–31]. These features endow coatings based on silica nanoshells with a low SHG and a desirable VLT in the same way as previously described for silica aerogels [25]. Furthermore, and unlike aerogels, no collapse of the pores takes place after contact with water. The structural preservation of mesoporous silica nanoshells, combined with their chemical stability, poor thermal conductivity, and high transmittance in the visible, render these nanostructures as an

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