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Sensing Properties of Metamaterials Utilized as Self-Cleaning Coating for Solar Mirrors

Towards the "Talking Mirror"

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Abstract. In this work the experimental activity conducted on self-cleaning sensitive metamaterial coatings for solar mirrors is described. The aim of the research activity is the modulation of solar mirrors wettability in order to reduce water consumption in ordinary cleaning operation and, consequently, maintenance costs, as well as the addition of sensoring properties to the mirrors for the remote acquisition of their performance. In particular, cermet metamaterials and hybrid polymers have been selected as matrices and doped with conductive particles. Considering that in the most part of solar mirrors architectures the external layer consists of an amphiphobic alumino-silicate, which has a wetting contact angle (WCA*) of around 50°, in this work different “silica-like” based coatings have been fabricated by means of sputtering deposition (for inorganic cermet metamaterials) and spraying (for polymers) with the aim of obtaining a more hydrophobic behavior (WCA > 90° can halve the amount of water required for mirrors cleaning), preserving mirrors optical properties and exhibiting, at the same time, electrical properties suitable to sensoring purpose.

Keywords: Self-Cleaning Coatings, Solar Mirrors, Sensors

1. Introduction

The reduction of Operating Expenses (OPEX) of Concentrated Solar Power systems is considered one of the main priorities in view of this technology deployment at commercial level [1]. Particularly, the maintenance of solar mirrors reflectivity, typically reduced by soiling [2], represents a relevant cost item, in terms of water consumption and personnel effort, especially for countries with high labor or resource costs (e.g. desert areas). The use of self-cleaning reflectors (mirrors coated with self-cleaning thin transparent films), that can be washed with limited amount of water, could significantly impact on the overall maintenance costs [3]. One of the main issues in the development of self-cleaning mirrors is to reduce the soling rate while withstanding degradation due to environmental factors and preserving optical transparency/reflectivity of the component [4]. Therefore, an emerging strategy for guaranteeing performance of solar mirrors throughout their entire lifetime consists in the integration of an autonomous and smart operational quality control, in addition to the deposition of self-cleaning coatings [5].

Providing a solar field with smart detection systems would allow not only to register the soling level, but also to identify possible failures in the mirrors and program cleaning operations and/or component substitution. From a practical point of view, this can be obtained by adding sensing properties to mirrors. In this regards, in a previous work, we demonstrated that it is possible to change wetting properties of solar mirrors applying transparent and auxetic metamaterials on reflectors surfaces by means of scalable processes, with the purpose of reducing water consumption in cleaning procedures [6]. In particular, auxetic nitrides obtained by sputtering deposition on metallized low iron glasses were proposed as self-cleaning solution ideal for back surface mirrors (BSM) [7], while hybrid organic-inorganic nanocomposites, deposited on a lab scale by spin coating and on a pre-industrial scale by spraying, were proposed for front surface mirrors (FSM). Both developed coatings were transparent, hydrophobic, and produced by means of cheap and scalable techniques onto large substrates, as shown in Fig.1 [8].

Figure 1. a) Auxetic nitride based sputtered coating deposited on 10x30cm BSM solar mirror; b) nanocomposite coating deposited by spraying on 50x50cm BSM solar mirror; c) nanocomposite coating deposited by spraying on 15x15cm adhesive FSM Refletec mirror.

Starting from these results, and considering that a great issue for maintenance operations of even coated solar mirrors comes from erosion and corrosion of surfaces exposed to the environment [9], in this work we propose to extend coatings requisites, formulating self-cleaning metamaterials that can have additional properties, for example the ability of acting as sensors of performance failures due to erosion, corrosion, soiling, humidity, and other possible factors (e.g. break events, ageing, etc.), as well as to provide, by means of a proper electronic inter-face and IoT, information about the operativity of single mirrors and/or of the entire solar field. To reach such an ambitious result, the first step is to make metamaterials conductive, in order to obtain resistive sensors that can change their conductivity depending on their operational state, evidencing significant performance loss or even a failure. Subsequently, solar mirrors could be covered (*in toto* or in part) with such an "intelligent" metamaterial, whose metallic nanostructures and quantities could be selected for meeting specific sensor requirements.

2. Results and discussion

In the followings, the fabrication and characterization of two self-cleaning coating formulations with additional sensing properties conferred by the insertion of conductive elements is de-scribed: 1) inorganic cermet metamaterials and 2) hybrid polymeric composites, containing conductive nanoparticles.

2.1 Inorganic cermet metamaterials

The inclusion of nanostructures (like Silicon, Zinc oxide, Aluminum, Silver, Tungsten, other conductive nitrides, etc.) into insulating sputtered matrices (silicates, nitrides oxy-nitrides) can change surface wettability (from 52° to 113° WCA) and make coatings conductive while pre-serving optical clarity (and hence specular reflectance of the mirror) with the aim of using them for sensing purposes. As an example of inorganic cermet metamaterial, we considered com-posites based on silicate matrices containing conductive zinc oxide and silicon nanostructures.

A composite consisting in silicon and zinc oxide nanostructures dispersed in an insulating matrix of silicates can be obtained by means of a solid state reaction carried out at comparatively low temperature (from 450 ◦C to 560 ◦C) between stratified nano-layers of zinc oxide and amorphous silicon deposited by magnetron sputtering. This original low temperature and scalable process can be considered very promising in nanocomposites fabrication technology. It promotes a multi-phase system of quantum dots (amorphous and crystalline silicon nano-aggregates, ZnO nano-crystals) whose composition can be tailored to fabricate self-cleaning coatings with electrical properties suitable for sensing purposes.

High annealing temperature, and/or long annealing duration, and/or thin sputtered Si and ZnO layers, are possible conditions that induce precursors consumption and formation of zinc silicates. Indeed, too low annealing temperature, and/or too short annealing duration, and/or too thick sputtered Si and ZnO layers, can lead to the formation of a composite containing not reacted Si and/or ZnO as nanoaggregate dispersed in the matrix.

Two main objective have been pursued in this work: 1) obtaining composites with defined optical and electrical properties; 2) obtaining a self-cleaning sensitive coating system (constituted by a matrix containing nanoparticles).To reach these two goals, different composites have been produced and characterized by means of FTIR, UV-VIS-NIR spectroscopy, micro-RAMAN, XRD, TEM, WCA measurements.

In Figure 2, cross-section observation of one representative composite by transmission electron microscopy X-TEM at an acceleration voltage of 200 kV is shown. In the pictures, alternate regions with different brightness are evident; by energy electron loss spectroscopy (EELS) their correlation with SiOx layers (clear regions) and zinc silicate layers (dark regions) is clarified. At the same time, inside SiOx layers crystalline, Si nano-aggregates are visible, whereas, inside silicate layers crystalline ZnO, nano-aggregates are evident. Both the types of nano-crystallites show different shapes, from spherical to ellipsoidal, with the smallest dimension of the grain size ranging from 4 to 7 nm.

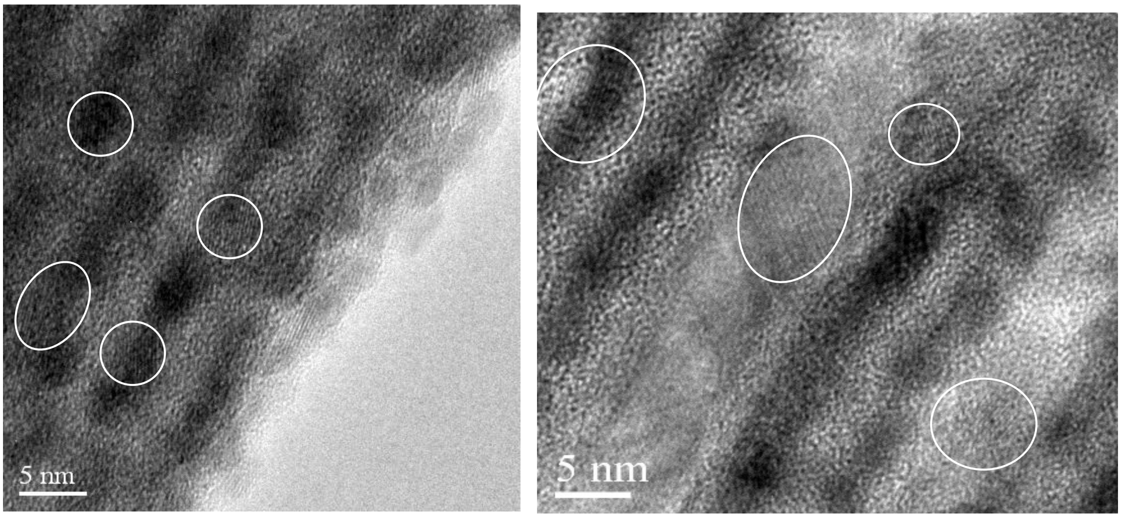

Figure 2. HRTEM of a composite containing Silicon and Zinc oxide conductive nanocrystals.

The above reported results obtained by TEM observation on composites can be illustrated in a schematic picture (see fig. 3). Particularly, zinc silicate composites can be described as Si nanocrystalline and amorphous (nc-Si, na-Si) and ZnO-nanocrystals (nc-ZnO) embedded in a hetero-superlattice (alternate layers of silica and silicate).

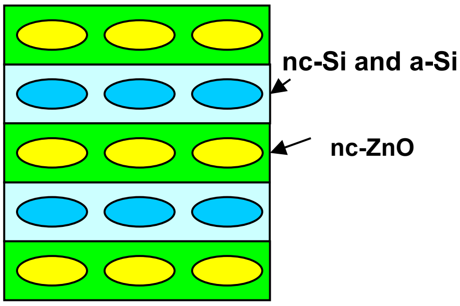

Figure 3. Scheme of the solid state reaction products.

In Table 1 electrical characterization of fabricated inorganic metamaterials, containing conductive zinc oxide inside a silicate transparent matrix, are reported.

Table 1. Electrical properties table of different conductive samples and relative WCA.

Sample	**ρ^l [Ω cm]**	**WCA(°)**
C-1000-400	16	97
C-700-400	67	76
C-1000-450	1.5	97.4
C-850-450b	5	96.8

To the purpose of obtaining electrical characterization of produced materials, the following configuration (Fig.4) of electrical measurement has been utilized.

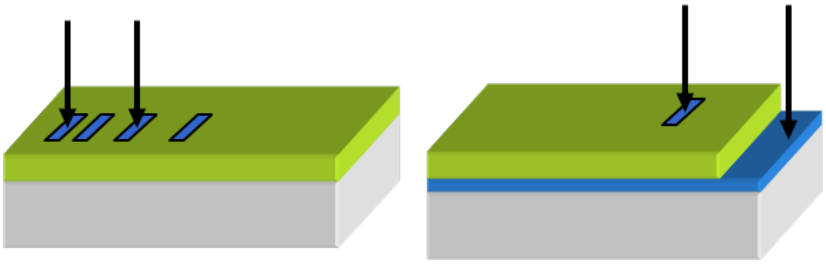

Figure 4. Scheme of electrical measurement: Resistivity measurement configurations: 1) opportunely distanced aluminium strips onto Metamaterial/ Glass structure (planar configuration) to measure lateral resistivity; 2) Aluminium strips onto Composite/Metal/Glass structure (sandwich configuration) to measure vertical resistivity.

Wetting Contact Angle (WCA°) and transmittance of one of such composites (sample C1000-400) is shown in Fig. 5.

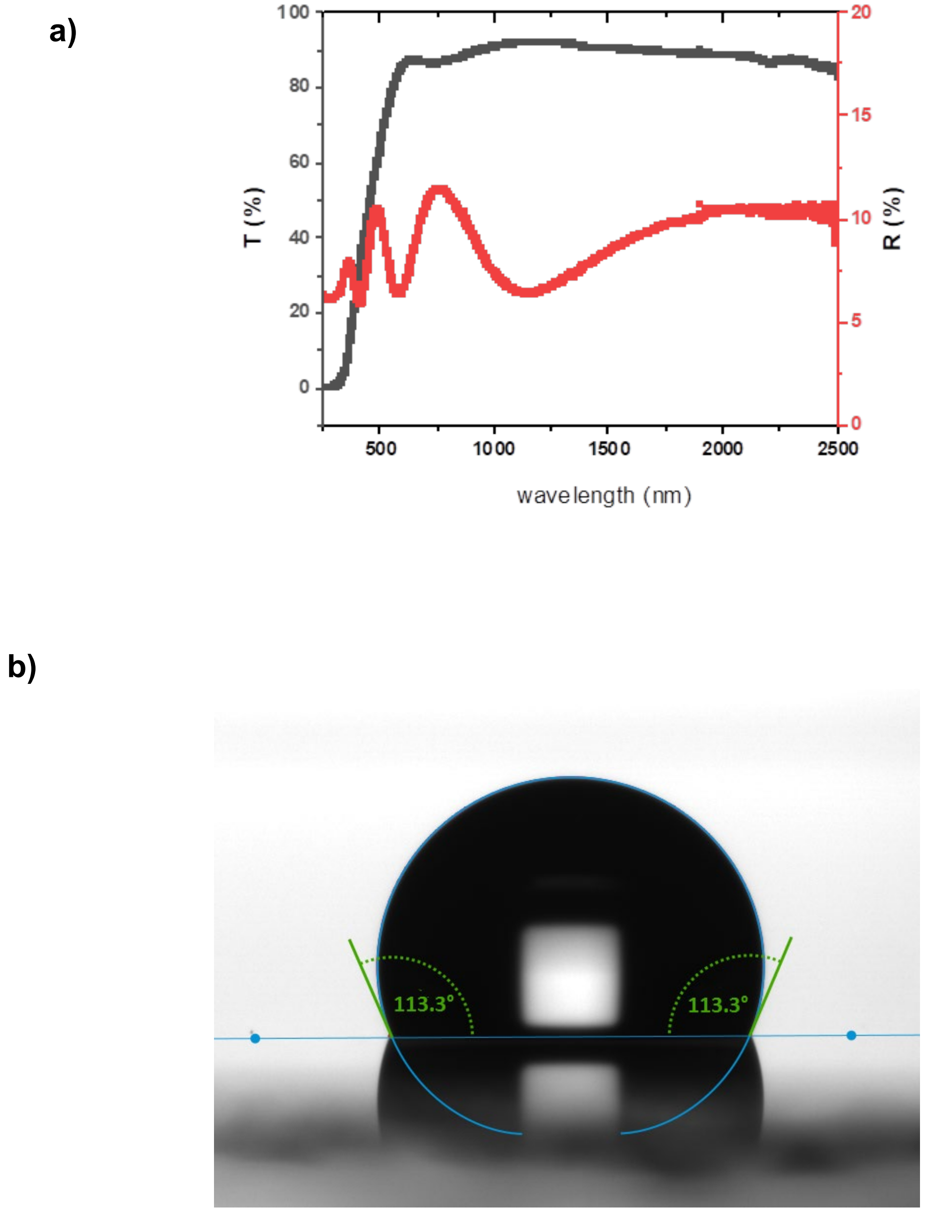

Figure 5. a) Transmittance and reflectance of C-300 on glass; b) Wetting angle measurement of C-300 (WCA=113°).

It is possible to note that both requisites are indicative of very good performance as transparent self-cleaning coating.

2.2 Hybrid polymers

Regrading hybrid polymers, a nanocomposite formulation has been proposed, whose nanostructured nature has been induced by anisotropic inorganic nano-sized guests into polymers for optic, combined to conductive fillers and/or organic molecules guesting. Even in this case, resulting metamaterials are hydrophobic (WCA>100°) and highly transparent (Fig.6a). Moreover, they can be conductive (Fig.6b) and their electrical behavior can be correlated to some interesting properties/information, like the "on field" transition temperature (related to aging of polymeric mirrors exposed to weathering), or the RH% (Fig.6c) electrical sensing (related to humidity level measured on the single mirror).

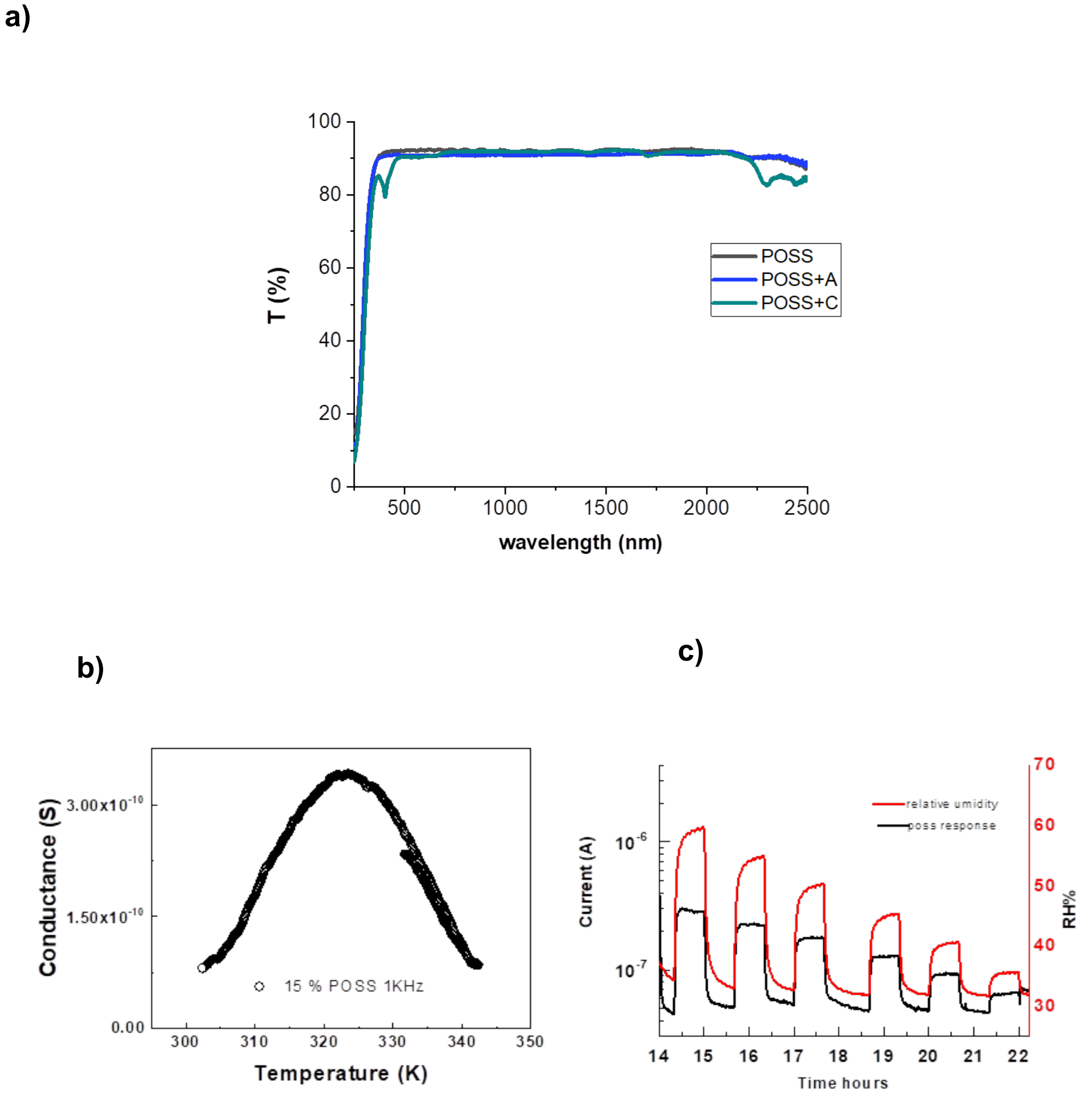

Figure 6. a) Hybrid composites visible transmittance in UV-VIS-NIR range. b) Conductance-temperature measurement of POSS. c) Dynamic response as a function of different steps of humidity, compared to commercial humidity probe sensor.

3. Conclusions and outlook

Self-cleaning transparent metamaterials have been tailored, produced on a lab scale, characterized, and proposed as solar mirrors coatings with potential sensing properties of different parameters (dust, humidity, erosion, aging, failure, etc.). Fabrication methods are cheap, scalable and could be easily integrated into already existing production lines of commercial solar mirrors. The work shows that it is possible to produce self-cleaning inorganic and hybrid coatings for solar mirrors by inserting conductive nanostructures inside their matrices that provide electrical properties useful for sensor development purposes. A similar original approach combines hydrophobic and sensitive effects to optical clarity and results promising toward the fabrication of a "talking mirror", that can give information about its performance, potentially contributing to a reduction of solar mirrors field maintenance costs. As a follow up of this work, an exhaustive experimental activity is already ongoing toward the scale-up at prototype/pre-industrial level of coatings devoted to the sensing of different parameters.

Author contributions

“Conceptualization, M.L., L.T., A.C., E.G.; methodology, A.C. and E.G.; data curation, E.G. A.C., G.V.; writing—original draft preparation, A.C.; writing—review and editing, A.C., M.L.

Competing interests

The authors declare no competing interests.

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