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A facile one-step method to fabricate multi-scaled solar selective absorber with nano-composite and controllable micro-porous texture

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ABSTRACT

A multi-scaled structured solar selective absorber (SSA), combining micro-porous texture and ternary nano-composite (carbon-dielectric-metal), was prepared by a facile one-step method in the frame work of sol-gel process. The textured surface has a crater-like pattern ranging from 0.2 to 2 μm, in which carbon-dielectric nano-composite serves as the thermal stable skeleton material to protect Cu and Cu_2O particles embedded inside the matrix. Complementary structure has been demonstrated by theoretical modeling and optical characterization to enhance the optical absorptance of SSA coating. The results indicated that the one-layer SSA with a pore size of around 1.1 μm presents an absorptance of about 0.8 and an emittance of about 0.08. Furthermore, the little deterioration after aging test for 50 h (at 100 °C in water vapor atmosphere and 500 °C in vacuum) highlights an outstanding durability, implying that such multi-scaled structured film is low cost, easy to large-area product, and capable of being an excellent SSA for the low-middle temperature applications.

1. Introduction

Over the past centuries, fossil fuels have fulfilled most of our energy requirements being more cost-efficient, but have also resulted in serious environment pollution [1]. Due to ever increasing demand of the green energy supply, growing attentions have been focusing for an abundant and sustainable energy source, *i.e.* solar energy [1,2]. Basically, there are two techniques to directly harvest energy from the sun 1) Photovoltaic (PV) solar cells, 2) Solar thermal collectors (STC). Despite the rapid development in PV industries, solar-thermal conversion technique still has its own advantages such as i) *Wide applications*: solar collector receiver temperatures range from 100 °C to 1500 °C according to different receiver systems [3], including various applications such as solar water heating, space heating and cooling, refrigeration, industrial process heat, desalination and thermal power generation; ii) *High efficiency*: compared with PV system, whose photo-electricity efficiency ranges from 10% to 25%, photo-thermal conversion efficiency in STC is much higher and, for commercial products, generally greater than 80% [4].

The main component in STC system is a functional film material called solar selective absorber (SSA), which could efficiently convert solar radiation into heat. This effective photo-thermal conversion is mainly attributed to two key optical features. *The high absorptive ability* in the solar radiation dominated region, *i.e.* ultraviolet to near infrared spectrum range, characterized by absorptance (α), given in the Eq. (1). Secondly, *the low* emittance (ε) in the middle-far infrared range, which prevents heat loss from the absorber through low heat radiation, is given in the Eq. (2).

$$\alpha = \frac{\int_{0.3\ \mu m}^{2.5\ \mu m} I_s(\lambda)(1 - R(\lambda))d\lambda}{\int_{0.3\ \mu m}^{2.5\ \mu m} I_s(\lambda)d\lambda} \tag{1}$$

$$\varepsilon = \frac{\int_{2.5\ \mu m}^{25\ \mu m} I_B(\lambda)(1 - R(\lambda))d\lambda}{\int_{2.5\ \mu m}^{25\ \mu m} I_B(\lambda)d\lambda} \tag{2}$$

where I_s is the intensity of solar radiation (AM 1.5, ASTM G173-03, ISO), R represents the reflectance of the sample, I_B is the radiation associated with blackbody at a given temperature. Since the radiations of I_s and I_B are generally separated far apart in the spectrum as shown in Fig. 1, the functional absorber is called "selective". According to the optical performance of an ideal SSA as depicted in Fig. 1, the totally opposite optical features in two spectrum ranges, standing for high α and low ε, could hardly be fulfilled by one intrinsic material. The fabrication of a tandem structure by depositing a thin black-like absorptive layer on a metal substrate has been established as a

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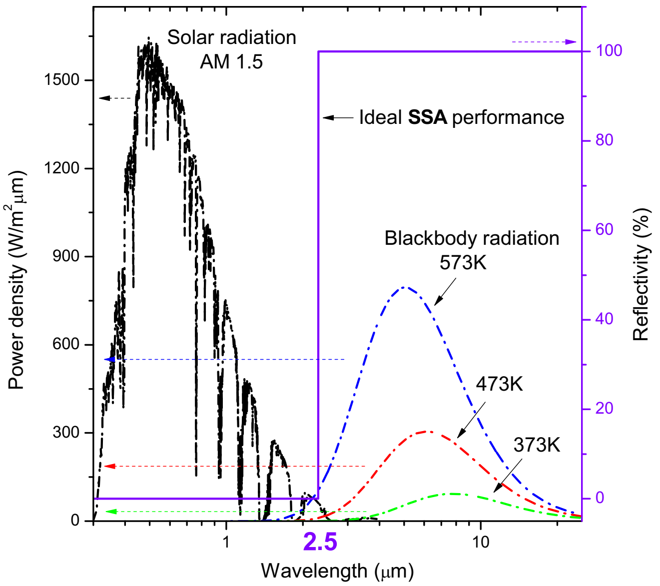

Fig. 1. The solar radiation (AM 1.5, ASTM G173-03, ISO), blackbody radiation at different temperature and the reflectance of an ideal solar selective absorber.

common strategy [5]. In this regard metal substrates, due to a high reflectance in the infrared range, could provide excellent low-emissivity while the additional black-like layer with low infrared absorption may help in obtaining remarkable absorptive ability in the visible range to achieve a high α value, note that ε of the tandem film should remain low.

Based on such tandem film design, numbers of solar selective absorbers have been developed and investigated to enhance the photo-thermal conversion [2,5]. Among those absorber films, two promising structures, namely textured surface and nano-composite, stand out. The former could create light-trapping morphology on the surface as shown in Fig. 2a, and the multiple-reflecting effects enhance the absorptive ability of the absorber [6]. However, a desirable surface texture is generally hard to be fabricated and involves expensive complex processes [6]. Another strategy to enhance the absorptance of SSA, displayed in Fig. 2b, involves nano-composite structures. This scheme mainly includes nano-cermets [7–11] and dielectric-carbon composites [12–16] films, relating to various nano-composite effects, such as localized surface plasmon resonance (LSPR) phenomenon, defect-induced energy level transition, Rayleigh scattering and Mie scattering. Despite a high bulk absorptive ability of such nano-composite SSA, the undesirable reflectance caused by smooth surface still needed to deal with, so that an anti-reflective layer is generally required on the top of nano-composite films. As a consequence, high-performance SSA fabricated by a facile approach is hard to be achieved by using only one of the strategies, unless coupling several strategies together, *i.e.* the complementary structure.

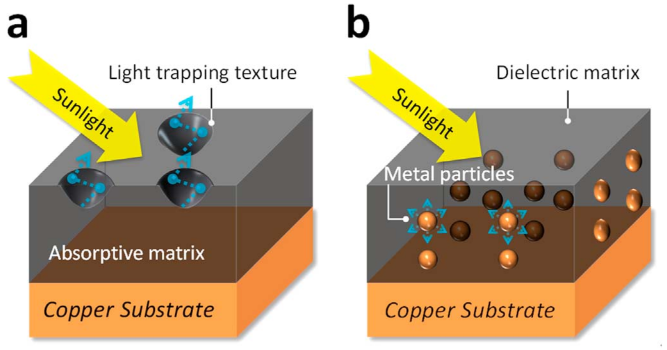

Fig. 2. The schematic diagram of (a) textured surface and (b) nano-composite structure.

Despite the well-known available approaches to fabricate complex film structure, *i.e.* lithography [17,18], photolithography [6] and laser interference metallurgy [19], Moon [20,21] recently proposed a ‘bottom-up’ route to prepare a multi-scaled SSA by compositing wide-range-particle-size semiconductor powders with dielectric matrix. Such a design scheme utilizes the concepts of the ‘intrinsic semiconductor’, ‘textured structure’ and ‘nano-composite’ films to achieve high solar selective absorption and thermal stability. They prepared multi-scaled semiconductor powders by a modified spark erosion process and then deposited the particles on stainless steel surface by a solvent method. The complementary SSA presented an outstanding absorptive-enhanced ability indeed. But the two-step process is less prone to regulate the film structure. The as-prepared SSA is about 10 µm thick dominated by the upper boundary of the multi-scaled powder size evidently too thick for an SSA coating [22]. Furthermore, the designable grading of semiconductor particles is also difficult to be managed. More recently, another design of multi-scaled-structure SSA has been provided, which combing copper oxide nano-wire (100–200 nm in diameter and about 5 µm in length) and cobalt oxide nanoparticles (100–200 nm in diameter) [23]. These complementary multi-scaled structured SSA exhibit a better solar absorption than single copper oxide nanowire or cobalt oxide nanoparticles. However, it still suffers few drawbacks such as time consuming process, poor controllability from the multi-step process, and deteriorated emittance from large thickness to achieve complementary structure. Hence facilely fabricating a practical complementary SSA still remains challenge, mainly due to the complexity of designing an ideal complementary scheme and processing such a controllable structure.

In the present work, we provide a high-performance SSA design scheme that combine ternary carbon-dielectric-metal composite film and controllable porous texture. These films can be fabricated by a facile one-step method in a framework of sol-gel process. In our proposed scheme, instead of conventional dielectric matrix, carbon-dielectric composite serves as the skeleton material, providing a better thermal stability and mechanical support [24]. Metal nanoparticles have been utilized as the nano-enhanced phases embedded in the composite matrix, generating nano-composite effects to improve the inside absorption [24]. Porous morphology on the SSA surface has been designed as light-trapping factor, which could enhance the absorption by multi-reflections. The numerical calculations and comprehensive experimental investigations have been carried out, getting insights into the composite films, and also demonstrated that the proposed strategy is theoretically and practically remarkable for solar selective absorber coating.

2. Theory and calculation

The theoretical assessment of the novel SSA film, with textured surface and nano-composite structure, is necessary and essential step carried out to verify the enhancement effects upon the absorptance. Four typical SSA film structures have been proposed and the elaborations of their optical constants as shown in Fig. 3a. The details of these four structures are depicted as the following:

1) *Carbon-dielectric matrix only (MO) film*: the optical constants of this film matrix was established on the basis of previous work performed on carbon-TiO_2 composite films [24], resulting in a relative high refractive index and moderate extinction coefficient.
2) *Matrix+nanoparticles (MN) film:* this nanocomposite film was treated as an effective homogeneous material by Bruggeman effective medium approximation (BEMA), of which the effective optical constants are the combination of MO film and separated metallic nanoparticles. The optical constants of nanoparticles were evaluated using a typical oscillator model [25,26] as also shown in Fig. 3a and the concentration of nanoparticles was set as 20%.
3) *Matrix+textured surface (MT) film*: the effective optical constants