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Solar selective absorbers with foamed nanostructure prepared by hydrothermal method on stainless steel

Xingli Wang, Xiaofeng Wu, Long Yuan, Cuiping Zhou, Yanxiang Wang, Keke Huang, Shouhua Feng

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, PR China

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ABSTRACT

Currently, solar absorber plays a key role among all components of the concentrating solar power (CSP) system, which is considered as an important way for solar energy utilization. Due to the outstanding features of surface texture, nano-structured materials have been extensively utilized for solar energy harvesting and conversion, but most of them were synthesized by expensive or complicated techniques. Herein, for the first time, solar selective absorbers with uniquely foamed nanostructure, are grown *in situ* by facile hydrothermal method on stainless steel, without using any porogen or template. The selective absorber films, which comprised a large number of nanoparticle agglomerates and nanopores, have a vital role on the solar selective absorptance owing to the increased optical path as well as enhanced sunlight trapping *via* foamed nanostructure. They show an excellent solar thermal performance with the solar absorptance and the thermal emittance of 0.92 and 0.12, respectively. Besides, the solar absorber films also exhibit considerable solar thermal performance and benign thermal stability at high temperature. Due to the relieving internal stresses from foamed nanostructure, there is no obvious cracking within the entire structure even after heat treatment. Consequently, the hydrothermal method used in the present investigation happens to be a novel, pollution-free, low-cost, and suitable for simultaneous mass production for large-size absorber films. Moreover, the pre-treatment of substrate and post-treatment of films are also very convenient and environmental, without any complex procedure. Accordingly, the resultant films with foamed nanostructure will have a good prospect as a new-family of solar selective absorbers, which may have a tremendous potential for industrial production in the future.

1. Introduction

Solar absorber plays a key role among all components of the CSP system, it absorbs solar radiation and then converts into heat. As for high-performance solar absorber, the key requirement is its spectral selectivity, namely a strong absorptance in visible-near-infrared region coupled with low emission in the infrared (IR) region [1,2]. Surface texturing is a common technique to obtain spectral selectivity by the optical trapping of solar energy [3]. In recent years, the application of nano-structured materials for solar energy harvesting and conversion has been gaining momentum [4–7]. Two and three dimensional (2D and 3D) periodic nano- or micro-structured surfaces were proposed to be alternatives for better spectral control [8–10]. The porous microstructures [11,12], tandem structures [13–16], needle-like structure [17] and branched nanowire forest [18] have been shown great superiority [19] owing to the increased optical path [5,11]. H. Sai et al. prepared 2D surface with submicron holes on tungsten substrates by fast atom beam etching [20]. Due to the standing wave resonance between the electromagnetic fields and the standing wave mode in the holes, this surface obtained the absorptivity of 0.82 and the emittance of 0.057 at 400 K. A. Lasagni et al. reported the surface structure on copper and stainless steel by laser interference metallurgy [21]. The resultant structure performed a desired spectral selectivity with the optimal absorptivity and emittance of 0.498 and 0.093 at 300 K, respectively. T. Kim et al. synthesized the tandem-structured layers of CuO nanowires and Co_3O_4 nanoparticles, which exhibited superior solar absorbing properties (figure of merit values is c.a. 0.90), the adhesion between the absorber and the substrate needed to be further improved yet [13]. So far, although lots of high-performance solar absorbers have been reported through plating, etching, magnetron sputtering and vapor deposition etc. However, many of them are often weakly adhesive, expensive, or multi-step, even need complicated equipment or high energy consumption in preparation. In previous reports [22–24], toxic chemical polishing agents such as acetone, isopropyl alcohol etc. were also always utilized in the pre-

E-mail address: shfeng@jlu.edu.cn (S. Feng).

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treatment of substrates. Thus, it is very important to introduce a convenient and environment-friendly strategy, that the pretreatment is facile and nontoxic and the solar selective absorbers are low-cost, firmly-adhesive and easy for large-scale preparation.

Stainless steel is widely used in solar heat collector for solar power plant. It has high thermal conductivities, the excellent corrosion resistance to working fluids, and contains transition metal elements such as Fe, Cr, Ni [23,25,26], whose corresponding oxides are common used for solar energy absorption material. Besides, the smooth surface of stainless steel plate generally has low emissivity. However, the poor solar absorption performance makes it unsuitable to be used as solar selective absorbers directly.

Hydrothermal method is an excellent strategy to prepare various materials with many novel structure and morphology due to its high temperature and high pressure [27]. Under normal temperature and alkaline condition, many kinds of stainless steel can be seldomly corroded. Hydrothermal condition may accelerate their corrosion processes [28], and obtain special nanostructure oxide surface. Herein, the Fe–Cr–Ni–Mo stainless steel was firstly utilized in NaOH solution by hydrothermal method to prepare the solar selective absorbers. These as-prepared foamed nanostructure absorbers, are grown *in situ* on stainless steel without the use of any porogen. They are constructed on the stainless steel surface firmly, and are composed of nanopores and nanoparticle aggregations. The as-prepared absorbers display a solar absorptance of 0.92 and a thermal emittance of 0.12 at 300 K. Thus, these films with self-assembled foamed nanostructure will be very promising for integration into the CSP devices.

2. Experimental details

2.1. Film preparation

Herein, Fe–Cr–Ni–Mo stainless steels were purchased from baoshan iron& steel, NaOH (AR grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used without further purification. Deionized water was used in all procedures of experiments.

As for film preparation, the stainless steel sheets were wiped with alcohol swabs and were not subjected to either chemical or mechanical polishing at first. Then they were placed into Teflon-lined autoclaves along with 15 M sodium hydroxide solution and the mixture was subjected to hydrothermal treatment at 200 °C for 24 h. Finally, the films with foamed nanostructure could be obtained after ultrasound treatment, washing and drying.

2.2. Characterization method

X-ray diffraction (XRD) data were collected using a Rigaku D/Max 2500 V/PC X-ray diffractometer with monochromated Cu Kα radiation (λ=0.15418 nm) to identify the crystal structures of the films at a scanning rate of 6 ° min^{-1} in the 2θ range of 20–70°. The EDX and morphologies of the films were examined using field emission scanning electron microscopy (SEM) on a Helios NanoLab 600I from FEI Company. The cross sections of the selective absorber films were obtained by focused ion beam (FIB), and the measured micro area was protected by deposited platinum before being etched by gallium ion. EDX results for each film was measured for 6 times, and the average intensity was counted. Reflectance in the wavelength interval 0.3–2.5 μm was measured by a Perkin-Elmer Lambda 950 UV/vis/NIR double beam spectrophotometer equipped with an integrating sphere. Over the infrared range 2.5–20 μm, a Fourier transform infrared reflectance (FTIR) spectrometer TENSOR 27 (Bruker Optics) was used, which was equipped with an integrating sphere coated with gold.

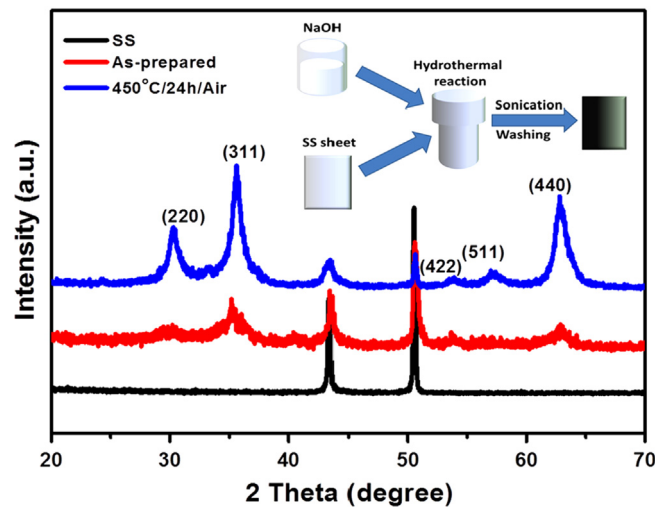

Fig. 1. XRD patterns of stainless steel substrate (black), as-prepared film (red) and the film heated in air for 24 h at 450 °C (blue). The as-prepared film is prepared by hydrothermal reaction for 24 h. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

3.1. XRD results

The diffraction profile of the selective absorber films (Fig. 1) have been successfully indexed to the Fe_3O_4 phase (JCPDS: 65-3107) [29], similar to spinel structure. In XRD patterns, the peaks (at 2θ=43.48°, 50.54°) represent stainless steel. The characteristic peaks (2θ=30.18°, 35.58°, 53.64°, 57.0°, 62.70°), marked with their indices ((220), (311), (422), (511), (440)), are coincided with spinel structure as Fe_3O_4. Peaks of the as-prepared film have a small shift due to the doping of other elements (Cr, Ni) into the crystal lattice. This was in agreement with the energy dispersive spectra (EDS) and mapping analysis. We also note that the characteristic peaks of as-prepared film are broadened as a result of the nano-sized agglomerations on the film surface. After heating in air for 24 h at 450 °C, characteristic spinel peaks become narrower and sharper, owing to the sintering of the nano-agglomerates leading to larger particles and strong crystallization.

3.2. Morphology of the films

Surface and cross-sectional SEM images of the as-prepared film and the heat-treated (24 h @ 450 °C) film are shown in Fig. 2. The surface of the as-prepared film appears a typical foamed nanostructure, with a large amount of nanopores distributed in the surface uniformly (Fig. 2a1), it also can be seen that the supports of the foamed nanostructure are assembled by nanoparticles with the size of 30–40 nm from the enlarged view (Fig. 2a2). The cross-sectional image (Fig. 2a3) clearly shows a well-defined foamed nanostructure, the thickness of the layer is 2.32 um (The calculated thickness of the sample is based on the measured length under 52° tilted, the film surface is impregnated by some platinum as a protecting layer). The number and volume of the pores on film surface are reduced after 450 °C treatment for 24 h (Fig. 2b1), mainly due to the obvious aggregation of nanoparticle agglomerations as shown in Fig. 2b2. The roughness root mean square (RMS) of the untreated and 24 h @ 450 °C treated films are 4.077 nm and 9.317 nm, respectively. The cross section confirmed that the pores are reduced in the number and volume, and the foamed nanostructure is weakened (Fig. 2b3). There is no sharp interface between the *in-situ* grown foamed layer and the stainless steel substrate, implying a well bonding even after high