

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat



Black oxide nanoparticles as durable solar absorbing material for high-temperature concentrating solar power system



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ARTICLE INFO

Article history: Received 24 August 2014 Received in revised form 15 November 2014 Accepted 2 December 2014 Available online 8 January 2015

Keywords: Concentrating solar power Solar absorber Cobalt oxide Light trapping High temperature

ABSTRACT

Concentrating solar power is becoming an increasingly important part of the renewable energy portfolio. However, further cost reduction is desired to make CSP competitive with traditional energy technologies. Higher operating temperature is considered an attractive avenue leading to higher power conversion efficiency and lower cost, but tremendous technical challenges exist with higher temperature operation of CSP, with one of the main issues being the lack of a high-performance solar absorbing material that is durable at 750 °C or above. In this work, a black oxide material, made of cobalt oxide nanoparticles, is synthesized and utilized as a high-temperature solar absorbing material. The nanoparticles are embedded in a dielectric matrix through a scalable spray coating process. The top layer of the coating is further improved with light-trapping structures using sacrificial fillers introduced from the same coating process. After the surface modification of cobalt oxide coating, we achieved a high thermal efficiency of 88.2%. More importantly, the coating shows no degradation after 1000-h annealing at 750 °C in air, while the existing commercial light absorbing coating was reported to degrade by long-term exposure at high temperature. Our findings suggest that the materials and processes developed here are promising for solar absorbing coating for future high-temperature CSP systems.

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1. Introduction

The development and deployment of renewable energy sources is becoming an increasingly urgent need for human society [1,2]. Concentrating solar power (CSP) systems (or solar thermal systems) are becoming an important part of the major portfolio of renewable energy generation. One of the key potential advantages of CSP over many other forms of the renewables is the possibility of inexpensive energy storage using thermal energy storage systems (TES), which is useful for grid-level power management [3]. The TES can extend the electricity generation capability to periods with no sunlight available, thereby significantly expanding the value and usage of solar energy [4]. CSP systems can also be hybridized with other alternative energy systems, such as solar photovoltaic [5], thermoelectric [6,7], or thermophotovoltaic [8,9] systems, to increase the penetration of renewable energy power [10,11]. Despite these perceived benefits, the levelized cost of

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http://dx.doi.org/10.1016/j.solmat.2014.12.004 0927-0248/© 2014 Elsevier B.V. All rights reserved. energy (LCOE) of CSP, however, is still too high to compete with traditional thermal power plants and some other alternative energy technologies (such as photovoltaics) [12].

In order to develop a cost-competitive CSP technology, it is imperative to increase the system power conversion efficiency. To maximize the efficiency of CSP, it is desirable to raise the operating temperature for higher Carnot efficiency. As a result, the temperature of heat transfer fluids (HTFs) needs to be 700 °C or higher [13]. Toward this aim, all of the components of CSP systems, such as solar field, HTFs, power block, TESs, and solar receivers need to be made compatible with the higher-temperature operation.

As far as the solar receiver is concerned, the light-absorbing coatings on the receiver play an important role by absorbing solar thermal energy and raising the temperature of the HTFs to above 700 °C. Although spectrally selective coatings (SSCs) with multi-layers/graded cermets or tandem structures have been developed and stably operated in vaccum in parabolic trough CSP systems [14–19], none of these SSC structures can operate at high temperatures in air, which is needed in future solar-tower based CSP systems. The state-of-the-art solar absorbing material used in solar towers is based on a commercially available black paint called Pyromark 2500[®]. Pyromark 2500[®] is known to have high thermal efficiency above 600 °C and has been used for central solar receivers

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of CSP plants. However, according to prior studies, the absorptivity degraded after high temperature (> 700 °C) exposure due to crystal structure changes and phase instability [20,21]. Therefore it is clear that a new light absorbing coating material with high absorption efficiency and excellent durability at elevated temperature in air environment needs to be developed for the next generation CSP systems.

Since the light absorption is directly related to solar energy generation efficiency, a large number of studies about optical absorption enhancement have been actively pursued. Several light trapping approaches were studied, such as texturing [22–25], metallic nanostructures [26], and photonic [27–29] and plasmonic structures [30,31]. However, most of these studies about light trapping have been applied on photovoltaic applications using vacuum deposition methods. As a result, these processes are not necessarily compatible with CSP applications, where spray coating is generally employed to coat the light absorbing layers [21,32] onto solar tower receivers, for example, Pyromark 2500[®] in Solar One and Solar Two central towers [33,34].

Here, we report a highly efficient and high-tempeature durable light absorbing coatings based on cobalt oxide nanoparticles for CSP receivers. Cobalt oxide materials have been studied as selective absorbing layers and fabricated using spray pyrolysis method [35–37], chemical vapor deposition [38] and electrodeposition. Although several previous studies showed the applicability as solar collectors within the temperature range of 300-650 °C [39-41], there is no existing light absorbing coating suitable for CSP operating at higher temperature (\sim 750 °C) without performance degradation. In this study, the cobalt oxide nanoparticles were synthesized via a facile hydrothermal process and utilized as the light-absorbing material in the coating layers. The coating lavers consist of cobalt oxide nanopowders dispersed in silica matrix, and are deposited on metal substrates via a simple and scalable spray coating process, which is compatible with CSP applications. We employed novel and yet simple surface texturing techniques, based on sacrificial polymer beads that can be easily integrated with the spray coating process, to improve the light absorption. Finally, the developed coating layer exhibited unprecedented high-temperature durability, showing no degradation in structural or optical properties after annealing at 750 °C in air for 1000 h.

2. Experimental

2.1. Cobalt oxide nanoparticle synthesis and sample preparation

We first aimed at synthesizing cobalt oxide nanoparticles of right sizes for high light absorption. For nanoparticles (aspect ratio \sim 1), the optimal size for absorbing visible and near infrared light is probably around 200–400 nm [42]. If the particle size was too small, the resultant coating film would have small surface roughness, which is not effective for light trapping. In addition, for high temperature application, very small nanoparticles (< 100 nm) would agglomerate and become larger size particles. Therefore, we aimed at producing nanoparticles with hundreds of nanometers in diameter. Metal oxide nanoparticles can be prepared by a number of different methods, such as sol-gel technique [43], mechanical grinding (ball milling) [44], mechanochemical synthesis [45], and hydrothermal synthesis [46], etc. Here we utilized the hydrothermal method to synthesize Co₃O₄ nanoparticles for convenience. However, it should be noted that other inexpensive nanoparticle synthesis techniques mentioned above may also be used for producing metal oxides for SSC applications.

Cobalt oxide nanoparticles were synthesized via a hydrothermal process using cobalt chloride salt (CoCl₂•6H₂O) as the precursor. 10 M

solution of sodium hydroxide (NaOH) was gradually dropped into 1 M solution of cobalt chloride to induce precipitation of cobalt hydroxide until pH value of the reacted solution reached 11. The hydrothermal synthesis was performed at 150 °C for 20 h in order to transform the precipitated cobalt hydroxide into cobalt oxide. The cobalt oxide particles were then washed with de-ionized water using a centrifuge and dried using a freeze-dryer. The as-synthesized nanoparticles were annealed at 750 °C for 2 h for phase stabilization.

For the fabrication of Co₃O₄ slurry, methyl phenyl polysiloxane resin (SILIKOPHEN[®] P 80/X) was utilized as precursor of SiO₂ matrix. The volume ratio between the active material (cobalt oxide nanopowders) and the SiO₂ matrix was systematically varied and optimized. The required amount of resin was diluted with an organic solvent mixture consisting of two miscible solvents, xylene and isobutanol (volume ratio 3:1). The optimum dilution was important to ensure good quality of the coating layers, because too viscous slurry could not make a smooth spray stream while very dilute slurry could not make a stable spray-coating onto substrates. In order to dissolve the resin in the solvent, the mixture was sonicated for 30 min with a probe type sonicator. During sonication, the solution container was cooled in an ice-bath to avoid concentration change due to the evaporation of organic solvents. Co₃O₄ powders were mixed with the prepared solution and yttria stabilized zirconia (YSZ) grinding balls were also added into the blend. The ball milling was conducted for 24 h in order to make the mixture homogeneous.

The black oxide spray coating was performed using a spray gun on a high temperature Ni alloy (Inconel 625) sheet coupons ($\frac{1}{2}$ in $\times \frac{1}{2}$ in size). The spray pressure was set at 40 psi and the distance between the spray gun and the Inconel substrate is about 10 cm, which has been optimized for the best coating quality. After spray coating, the samples were heated at 250 °C for 1 h for curing of SiO₂ resin. All of the coating samples consist of two layers: the base layer of approximately 30 µm thick and a top layer with surfacetopography-modified structure described in the next paragraph.

2.2. Cobalt oxide surface texturing

The first method to alter the surface texturing and topography of the top layer to improve optical absorption was to employ imprinting stamps with SU-8 polymer pillars which were prepared by using standard microfabrication processes. The polymer pillars were 3 μ m in both diameter and spacing and 10 μ m in height. The stamps were then pressed onto coated Co₃O₄ coating surface and left as imprinted prior to the resin curing step. Then, the sample was annealed at 750 °C for 1 h to burn away the remaining polymer pillars.

The second method employed to create roughened surface is by incorporating and subsequently removing micron-sized sacrificial polymeric beads within the Co_3O_4 coating layer. The volumetric concentration of Co_3O_4 , polymer beads and silicone resin was optimized to yield the best optical performance (as shown in Table 1), and the mixtures were again sonicated with a probe type sonicator for proper mixing. Then, a desired amount of silicone resin was added, followed by the same ball milling and spray coating processes described in the prior paragraphs. Finally, the

able 1							
ample	fabrication	condition	and	figure	of	merits	(FOM).

Sample	Volume ratio	FOM (figure of			
name	Co ₃ O ₄ nanopowders	SiO ₂ dielectric matrix	Polystyrene polymer beads		
Co ₃ O ₄ -1 Co ₃ O ₄ -2 Co ₃ O ₄ -3	1 1 1	1.5 4.5 6.5	0 3 5	0.854 0.877 0.882	

coated layers were annealed at 750 °C for 1 h to remove the polymeric beads and leave behind the porous and topographically rough top surface of Co_3O_4 layer.

2.3. Optical performance and high temperature endurance evaluation

The thermal efficiency of a solar receiver, which measures the ratio of the energy absorbed relative to the incident solar energy, and FOMs can be calculated from Eq. (1).

$$F = \frac{\int_0^\infty (1 - R(\lambda)) I(\lambda) d\lambda - \frac{1}{C} [\int_0^\infty (1 - R(\lambda)) B(\lambda, T) d\lambda]}{\int_0^\infty I(\lambda) d\lambda}$$
(1)

where $R(\lambda)$ is the spectral reflectivity, $I(\lambda)$ is the spectral solar radiance per square meter as defined by the reference solar spectral irradiation (ASTM G173), $B(\lambda,T)$ is the spectral thermal emission of a black body at temperature T, and C is the concentration ratio. In the calculations used in this study, the black body temperature T of the solar receiver is assumed to be 750 °C and C is assumed to be 1000 (1000 sun), which are the target temperature and concentraion ratio, respectively, for enhanced efficiency of CSP systems. All of the integrals to calculate FOMs are evaluated in the range from 300 nm to $20 \mu \text{m}$, as only negligible quantities of solar power are present outside this range. Reflection data were measured at room temperature using a Labsphere[®] 4" integration sphere to collect all angles of reflection from samples and an Andor[®] 303i spectrometer equipped with a Si based (spectral range 300-1100 nm) and an InGaAs based (spectral range 900-2500 nm) detector. Reflection behavior of samples outside of the measured spectral range of 400–2.5 µm was extrapolated for use in Eq. (1). While the reflection data were measured at room temperature, it is highly desirable to obtain the reflection spectra at the actual operating temperature of \sim 750 °C. High temperature optical measurement in non-vacuum environment is highly challenging due to the heat conduction and possible damage to lenses, integration sphere, and other optical system parts. Such measurements will be attempted with improved design of the optical measurement system in progress, which will be reported in future publications.

To characterize the durability of the coating at elevated temperature, the long-time annealing tests at 750 °C in air were carried out on the coated samples as well as the Co₃O₄ nanopowders with the annealing time up to 1000 h. The composition of the material before vs after the annealing was analyzed using XRD (Bruker D8 Discover) using a scan speed of 0.037° s⁻¹ in the 2 θ range of 20–80°; the structural integrity was examined using an optical microscope and SEM (Phillips XL30 FEG); the thermal stability of Co₃O₄ phase at high temperature (750 °C) in air was also evaluated using thermogravimetric analysis (TGA, TA Instruments SDT Q600) with air of 20 ml/min flow rate; finally, the optical properties of the samples were measured with the same procedure as above.

3. Results and discussion

3.1. Cobalt oxide nanopowders synthesis and coating process

Cobalt oxide nanoparticles were synthesized by the hydrothermal process. Both the as-synthesized and annealed cobalt oxide nanoparticles were examined with scanning electron microscopy



Fig. 1. Cobalt oxide nanopowders characterization: (a) SEM image of as-synthesized powders and (b) X-ray diffraction pattern of Co oxide powders after stabilizing at 750 °C for 2 h, showing the Co₃O₄ phase.

(SEM). The diameter of the as-synthesized powders ranges from 100 to 300 nm after stabilizing heat treatment, as shown in Fig. 1(a). According to X-ray diffraction (XRD) analysis shown in Fig. 1(b), the synthesized chemical compound is confirmed as Co_3O_4 , which is one of the polymorphs of cobalt oxide [47,48]. Pure CoO is difficult to synthesize, because CoO can easily acquire oxygen and convert to a higher level oxide. While Co_2O_3 can be created when the cobalt compounds are annealed at a low temperature, it can easily be

converted to Co_3O_4 when heated above 538 K in oxygen-containing environment [49]. Therefore, we have concentrated our effort on the most stable form of cobalt oxide, i.e., Co_3O_4 . The coating process was carried out using a gravity-feed spray gun. All of the coating layers were deposited onto high-temperature Inconel substrate (type 625) coupons ($\frac{1}{2}$ in $\times \frac{1}{2}$ in area) pre-treated with sand blasting. Inconel was chosen because it is currently used for high-temperature CSP due to its high-temperature durability [50]. The schematic diagram



Fig. 2. (a) Schematic diagram of Co₃O₄ light absorbing coating structure and (b) photographs of a sand blasted Inconel-625 substrate and a Co₃O₄ coated sample (designated as Co₃O₄-1 sample).



Fig. 3. SEM images of (a) Co₃O₄ coating (scale bar: 5 µm) and (b) Co₃O₄ coating layer with 3 µm hole patterns (scale bar: 5 µm, inset, 20 µm) and the reflectance in the visible and NIR range of the two samples.

of the coated structure is shown in Fig. 2(a), and the photographs of a bare Inconel substrate and a sample coated with a Co_3O_4 layer are shown in Fig. 2(b).

3.2. Light absorbing coating structure modification

Fig. 3(a) and (b) shows SEM images of Co_3O_4 coating layer without and with embedded hole patterns (pores), respectively. The measured specular reflectance of the coating within the spectral range of 400 nm–2 μ m was shown in Fig. 3(c) and the FOM was calculated according to Eq. (1). The FOMs of the non-patterned and patterned coatings are 0.8542 and 0.8730, respectively. The suppressed reflectance due to the patterned sample led to $\sim 2.2\%$ increase in FOM, which is substantial and can be attributed to enhanced light trapping in the patterned holes. The incident light goes into the holes and diffracts at oblique angles within the Co₃O₄ absorbing coating, thus the light absorption is improved. Previously, computational and experimental studies [28,51-53] have shown similar optical light-trapping phenomena with various surface patterns, mostly with microscale pillars. Even though hole patterns may not be as efficient for scattering light in comparison to dense vertical pillar array structures due to the smaller surface area that an oblique light can reach, the process of making hole patterns is easier to implement with the spray coating process.

After establishing the principle of enhanced light absorption with surface hole patterning, we developed a more scalable process based on sacrificial polymer beads, as described in Section 2.2. The details of the samples are provided in Table 1. From the SEM images shown in Fig. 4(a) and (b), the surface roughness of the coating layer was increased after introducing the polymer beads in Co₃O₄ coating layer, compared to the original coating (Fig. 3(a)). The increased roughness results in reduced reflectance (Fig. 4(c)) and enhanced FOMs (Table 1). The FOM of the Co₃O₄-2 and Co₃O₄-3 samples are increased by 2.7% and 3.3%, respectively, compared to the initial Co_3O_4 sample. The roughened surfaces can be regarded as being close to the Lambertian surface, which is defined as a surface reflecting light with equal intensity in all directions, namely diffusely reflecting surface. Similar mechanism has been utilized for enhanced absorption in solar cells. for example, by creating 'black Si' using anisotropic etching of surface [22], hydrogen etching [54], or mechanical grinding [23,55]. Furthermore, random roughness helps to scatter light more efficiently than periodic structure due to a break in mirror symmetries (i.e. suppressed diffractive effects), as the prior simulation studies demonstrated the random or skewed pyramid structures outperformed regular pyramidal texturing [22,56]. Compared to these reported processes (etching or mechanical grinding), our process of using sacrificial polymer beads can be easily integrated with the spray coating process without any additional micromachining steps, with the polymer particles automatically burned away to create pores during the subsequent heating to the CSP operating temperature. Therefore, the process developed here is cost-effective and scalable to meet the needs of CSP applications. It is noted from Figs. 3 and 4 that there are reflectance peaks at about 1 µm and 1.8 µm wavelengths. These peaks are due to inherent optical properties of Co₃O₄. According



Fig. 4. SEM images of (a) Co_3O_4 -2 (volume ratio = 1(Co_3O_4):3 (polymer beads), see Table 1) coating (scale bar: 5 μ m) and (b) Co_3O_4 -3(volume ratio = 1(Co_3O_4):5 (polymer beads)) coating layer (scale bar=5 μ m) and the reflectance in the visible and NIR range of Co_3O_4 -1, Co_3O_4 -2 and Co_3O_4 -3 samples.

to Ref. [57], there are four absorption bands for Co_3O_4 in the visible to near-IR range: 0.83 eV (1.497 µm), 0.94 eV(1.322 µm), 1.7 eV(731 nm) and 2.9 eV (428 nm). These absorption peaks are associated with different charge transfer processes, as described in detailed in Ref. [57]. Because there is no absorption band immediately close to the 1 µm wavelength or above the 1.7 µm wavelength, the extinction coefficients are very small around 1 µm and beyond 1.7 µm [57]. As a result, these reflectance peaks at 1 µm and 1.8 µm are difficult to eliminate via surface patterning (Figs. 3 and 4). However, it is possible to remove these peaks by adding other compositions of metal oxide materials having absorption bands near 1 µm and 1.8 µm, which is a topic that warrants further investigation.

3.3. High temperature stability of Co_3O_4 light absorbing coating

The receiver coating in the next generation CSP systems should possess not only high thermal efficiency but also high temperature stability because of the anticipated trend of higher operating temperature (above 700–750 °C) [58,59]. The high-temperature stability of the coating depends on both the intrinsic material properties (e.g., phase transformation at high temperature) and structural integrity of the porous coating, as well as its adhesion to the substrate. We carried out the high-temperature annealing test in air as described in Section 2 for both the coating sample and the nanopowders. For the coated sample, the one with 1:5 volume ratio of cobalt oxide powders to polymer beads (Co_3O_4 -3) was used because it showed the best FOM in this study.

The microstructural and XRD analysis results are displayed in Fig. 5. Fig. 5(a) and (b) shows the SEM images of the nanoparticles after the 750 °C annealing in air. The images indicate that the surface roughness was not changed and the nanopowders were not agglomerated upon annealing, demonstrating the structural stability of the material. Fig. 5(c) shows the XRD results of the sample before and after the annealing. The XRD diffraction peaks for all the three samples (as-prepared, 100-h annealing, and 1000-h annealing) indicate that the samples consist of identical single phase Co₃O₄. The evaluation of phase stability of Co₃O₄ nanopowders at 750 °C in air was also made using TGA analysis as shown in Fig. 6, which shows that Co_3O_4 nanopowders gain weight by ~ 0.5 wt% in the process of temperature ramping up to 750 °C in air and the weight change becomes negligible (0 wt% change) during the annealing at 750 °C for 2 h. The initial weight gain is presumably due to the full conversion of residual CoO to Co₃O₄, after which the weight gain is essentially zero, showing the stability of the Co₃O₄ nanopowders. These results clearly show that the cobalt oxide nanopowders synthesized by the hydrothermal process in this study were stable at the set temperature of 750 °C. Cobalt usually forms two oxide structures, namely, CoO with NaCl crystal structure and Co₃O₄ with spinel structures [60]. According to the thermodynamic diagram of the Co-O system, Co₃O₄ is a stable phase at 750 °C in ambient atmosphere (0.21 atm O₂ partial pressure) [48]. In this environment, Co₃O₄ is stable from room temperature up to 840 °C and converts to CoO above 840 °C.

Finally, we show the FOMs of the best-performing samples with 1:5 volume ratio of black oxide powders to polymer beads



Fig. 5. (a, b) SEM image of Co_3O_4 coating after annealing at 750 °C for 1000 h (scale bar: (a) 5 μ m and (b) 1 μ m) and (c) XRD patterns of Co oxides, as-made (black), after 750 °C exposure for 100 h (red) and 1000 h (blue), showing no phase degradation after the annealing. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 6. TGA analysis results on Co₃O₄ nanopowders with temperature ramping rate of 20 °C/min followed by holding at 750 °C for 2 h under air-flowing. The initial weight gain is presumably due to the full conversion of residual CoO to Co₃O₄, after which the weight gain is essentially zero, showing the stability of the Co₃O₄ nanopowders.



Fig. 7. Figure of merit of two samples of Co₃O₄-3 described in Table 1 as a function of exposure time (up to 1000 h) at 750 °C in air.

(designated as Co₃O₄-3A and Co₃O₄-3B samples) after various annealing durations ranging from 0 to 1000 h in Fig. 7. The result clearly demonstrates that the FOM remains the same after 1000 h of high temperature exposure, indicating that the main features of the high optical performance, including cobalt oxide phase composition, surface roughness and porous structure were still intact after extended annealing. Therefore, Co₃O₄ black oxide is a promising solar absorption candidate material for 750 °C CSP operating environment. In contrast, Pyromark coating, which is the state of the art coating for CSP applications, shows $\sim 3\%$ degradation of solar absorptance at 750 °C after 300 h [21].

4. Conclusion

In summary, we have synthesized Co₃O₄ black oxide nanoparticles using a facile hydrothermal process and developed novel designs and fabrication processes of light-absorbing coating structure for hightemperature CSP systems. By introducing sacrificial polymer fillers into the nanopowder-based coating slurry, the surface texturing was successfully obtained and the optical performance was enhanced, as measued by a high figure of merit of 88.2%. For high temperature durability, a long-term aging test was performed and the results revealed that the light-trapping structure remained intact after 750 °C exposure in air for 1000 h. Consequently, the FOM showed negligible change after the 1000-h exposure. The findings suggest that the textured Co₃O₄ coating is a promising candidate for solar absorbing in next-generation high-temperature CSP systems. The Co₃O₄ layer can easily be spray-coated in a manner suitable for large-scale CSP receiver applications.

Acknowledgements

This work is supported by US Department of Energy, SunShot Program Contract no. DE-EE0005802.

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