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Copper-alloyed spinel black oxides and tandem-structured solar absorbing layers for high-temperature concentrating solar power systems

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Abstract

Although renewable solar power plants are rapidly proliferating, high cost and the intermittent availability of solar power are still significant barriers for its penetration into the energy grid system. Concentrating solar power (CSP) offers an attractive alternative due to its integration with cost-effective thermal energy storage systems. To further reduce the cost of CSP, it is imperative to operate the plants at higher temperatures for enhanced efficiency. One of the key components for next-generation high-temperature CSP is the solar absorbing coating materials. In this work, we have developed tandem-structured solar absorbing layers with $CuFeMnO_4$ and $CuCr_2O_4$ black oxide nanoparticles (NPs). These tandem structures exhibited a remarkably high solar-to-thermal conversion efficiency, or figure of merit (FOM), of 0.903, under the condition of 750 °C operating temperature and a solar concentration ratio of 1000. More importantly, the coating showed unprecedented durability, as demonstrated from long-term isothermal annealing at 750 °C in air as well as rapid thermal cycling between room temperature and 750 °C. Our results suggest that the tandem black oxide coating is suitable to meet the stringent demand of next-generation high-temperature CSP systems. The coating materials synthesis, structures, optical as well as thermal properties will be discussed.

Keywords: Spinel black oxide nanoparticles; Solar absorbing coating; Tandem structure; Porous surface; Concentrating solar power

1. Introduction

Electricity generation is accomplished by various ways including conventional power plants based on coal, natural gas, nuclear, and hydroelectricity, as well as renewable power plants including geothermal, biomass, wind, solar photovoltaic (PV) cells, and concentrating solar power (CSP) plants Turner, 1999; Varun et al., 2009; Khamwannah et al., 2012; Ho and Iverson, 2014; Hayman et al., 2008. In 2012, electricity generation from the renewable sources in US amounted to ~13% and it is anticipated to grow up to 18% in 2040 according to the projection of US Energy Information Administration (EIA) Levelized Cost and Avoided Cost of New Generation Resources, 2014. When estimating levelized

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cost of electricity (LCOE) in 2019, solar thermal electricity generation such as concentrating solar power (CSP) systems will still be around 3 times higher in LCOE than nuclear power plant and wind power plant (Levelized Cost and Avoided Cost of New Generation Resources, 2014). To make CSP cost effective, US Department of Energy (DOE) targets to reduce the LCOE of CSP to 6 ¢/kW h by 2020 which is ~30% of the LCOE in 2010 (21 ¢/kW h) Tackling Challenges in Solar, 2014. To reach this target, it is necessary to develop advanced materials and structures to improve the performance and reduce the cost of CSP systems. Among various components of a CSP system, the solar absorber is a critically important element. Solar absorbers are typically made of metallic alloy tubes, inside which heat transfer fluids (HTFs) are heated up by the absorbed solar energy to generate high-pressure steam for power generation (Burhardt et al., 2011; Moon et al., 2014). To enhance the solar absorbing capability, the tubes are usually coated with spectrally selective coating layers (for parabolic trough systems) or solar absorbing layers (for solar towers) Burhardt et al., 2011; Moon et al., 2014; Behar et al., 2013. To reach the DOE target, the following conditions on solar absorbers have to be achieved: HTF exit temperature $\geqslant$650 °C, solar to thermal efficiency $\geqslant$90%, and lifetime $\geqslant$10,000 cycles (Tackling Challenges in Solar, 2014). However, solar absorber temperature of today's tower type CSP plant is around 550 °C. As the efficiency of Carnot cycle type thermal device can be substantially increased by higher temperature operation, it is highly desirable to obtain a new solar absorber coating material that can withstand higher temperature exposure (such as 750 °C or higher) with long-term stability of structures and optical and thermal behavior.

Conventional solar receivers in solar tower plants are coated with a commercially available black paint named Pyromark. Pyromark-coated samples on Inconel 625 substrates showed degradation after 300 h isothermal annealing at 750 °C in air, as reported by Sandia National Laboratories (Ho et al., 2014). In order to increase the FOM, multi-layered solar absorbing layers have been developed using metal thin films with low IR emission (Kennedy, 2002). However, this type of tandem structure with metal films can only be used in vacuum or under inert environment as in parabolic troughs, and is not suitable for high-temperature solar towers because it can be easily oxidized in air.

The scientific and engineering challenges of achieving simultaneous high solar absorptivity and high temperature durability lie in the difficulty of ensuring stability of structures and optical properties of metallic, ceramic or carbon based absorber materials at high operating temperatures (e.g. 750 °C or higher) in air. Sturdy structures with nanoscale features can promote light trapping, diffuse and react optically well below their bulk melting point. Furthermore, multilayer thin film structures are prohibitively expensive to deposit on large surface area (hundreds of square meters per solar tower) in solar thermal plant structures. Also, the use of exotic nanopattering for improved light absorption or the use of nanophotonic structures will be too costly for solar thermal plant applications.

In this work, we overcome these challenges by adopting a number of novel strategies to demonstrate a new black oxide nanoparticle structure that is easy to produce by a simple spray coating process, exhibiting superior thermal stability and optical performance at high temperature. First, we synthesized spinel type (AB_2O_4) copper-alloyed black oxide nanoparticles. Spinel metal oxides have been attractive to thermal applications because of their oxygen stoichiometry and crystal structure stability at high temperature (Ambrosini et al., 2011; Vince et al., 2003; Bayon et al., 2008). Second, we utilized a two-layer tandem structure, consisting of a top layer of Cu–Fe–Mn oxide for absorption in the visible and near-infrared (IR) spectrum and a bottom layer of Cu–Cr oxide responsible for near-IR absorption. Finally, we employed a highly scalable spray coating technique that created porous surfaces for efficient light trapping (Moon et al., 2014; Peng et al., 2005; Tsakalakos et al., 2007; Zhu and Cui, 2010; Kelzenberg et al., 2010). By combining these novel features, as shown schematically in Fig. 1(a), our two-layered black oxide samples exhibited a high FOM and high-temperature durability.

2. Materials and methods

2.1. Synthesis of spinel Cu-alloyed metal oxide nanoparticles

Two types of black oxide nanoparticles with spinel structure were synthesized hydrothermally utilizing the co-precipitation method modified from what was reported in our prior publication (Kargar et al., 2015). For the synthesis of copper chromates, 1 M of copper chloride ($CuCl_2{\cdot}2H_2O$) aqueous solution was mixed uniformly with 1 M of chromium chloride ($CrCl_3{\cdot}6H_2O$) aqueous solution with vigorous stirring for 5 h, followed by co-precipitation into Cu–Cr hydroxides by addition of 10 M NaOH into the solution. After mixing the co-precipitated hydroxides for 2 h, hydrothermal synthesis was carried out in a 45 mL autoclave with a Teflon liner at 200 °C for 20 h. During the post-treatment, centrifuged particles were dried with a freeze-dryer and finally crystallized at 550 °C for 5 h or 750 °C for 2 h in air. With this procedure, copper chromates with two different compositions were synthesized, namely 1:1 and 1:2 in atomic ratio of Cu/Cr.

In the case of the spinel Cu–Fe–Mn oxide, the overall synthesis procedure was the same as that of copper chromates, except that the precursor solutions were made of the mixture of 1 M copper chromite ($CuCl_2{\cdot}2H_2O$), 1 M iron chloride ($FeCl_3{\cdot}6H_2O$) and 1 M manganese chloride ($MnCl_2{\cdot}4H_2O$) aqueous solution with different volumes depending on the atomic stoichiometry of Cu–Fe–Mn oxides. Cu–Fe–Mn nanoparticles with different compositions were synthesized, including 1:1:1, 0.5:0.5:2.0,