Synthesis of Copper Oxide Thin Film Via Sol-Gel Dip-Coating Route For Spectrally Selective Absorber Material

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ABSTRACT

Copper oxide thin film coatings have been successfully coated on reflective aluminium substrates via facile sol–gel dip-coating route for spectrally selective absorber (SSA) application. For quantitatively analysis, the reflectance spectra obtained from UV-Vis-NIR and FTIR equiped with the integration spheres were used to measure the absorptance and emitance values, respectively. To optimize the performance, relevant parameters such as the concentration of sol precursor and the dip-drying cycle were investigated. The increase of the concentration of copper sol precursor in range of 0.1 - 0.3 M increased the absorptance value, likewise with the increase of the dip-drying cycles. The maximum absorptance of α=72% with a spectrally selective absorber profile was achieved by a SSA material synthesized using 0.3 M copper nitrate, 0.3 M propionic acid, and 8 times dip-drying cycles. The emitance value of ε=6.63% for this coating was recorded. Good optical performance of spectrally selective absorber and the operational simplicity of the synthesis process make this coating have high prospect as spectrally selective absorber material.

Keywords: copper oxide thin film; sol-gel dip-coating; absorptance – emittance, optimization

1. INTRODUCTION

There are, at least, two approaches to convert solar radiation into electricity, namely direct approach using photovoltaic (PV) devices and indirect approach using photothermal conversion. Photothermal collectors convert solar irradiation to the heat, which is in turn, will be converted into electricity through the thermoelectric generator (TEG) or power steam generator (concentrator solar power (CSP). The efficiency of photothermal conversion is widely known much higher compared to photovoltaic [1]. Other applications for solar thermal collector are for solar water heater, solar air conditioner (solar AC), hybrid solar photothermal-photovoltaic (PV/T), solar dryer, etc. The key component of solar thermal collector is the solar-absorber surface which strongly affects the efficiency of the solar thermal conversion. Ideally, the surface absorps as much as possible incoming solar (UV-Vis_NIR) radiation (high absorptance) but rejects

the mid-far infrared (MFIR) to minimize heat loss from the heated surface (low emittance) or welknown as spectrally selective absorber (SSA) surface.

Most widely-used industrial SSA in recent years are metal particles in ceramic (cermet) structures produced by electroplating/electrochemical or sputtering/vacuum deposition methods. However, the electrochemical/electroplating processes are not environmentally friendly [2] while sputtering/vacuum deposition processes are technically complicated and necessitates high cost [3]. There is, therefore, a need for cost-effective and environmentally-friendly production of high quality SSA materials. In this context, sol-gel techniques meet these criteria and they are potentially very promising techniques. The sol-gel methods are well-known, simple, low cost, and environmentally friendly thin film fabrication techniques resulting in a uniform chemical thin film composition.

Cobalt copper oxides ($Cu_xCo_yO_z$) are versatile materials which have been used in a number important catalytic reactions such as conversion of syngas to higher alcohols [4, 5], oxidation of carbon monoxide (CO) by O_2 [6], oxygen evolutions reaction (EOR) [7], for Fischer-Tropsch synthesis [8] and for thermoelectric power generation material [9]. Numerous studies have been conducted to characterize the physicochemical, magnetic, conductivity, electrochemical and thermal properties of copper-cobalt oxides. However, solar-based optical properties of copper-cobalt oxides thin film coating are comparatively less studied [7]. In previous work we have synthesized the copper cobalt oxide based SSA [10, 11] using simple and environtmentally sol gel process. Our SSA coating showed promising material for spectrally selective absorber coating application.

For cost minimizing, stand alone copper oxide is worth considering. Some researches have explored the copper oxide spectrally selective absorber material, even though they were produced using a not environtmentally friendly processess [12, 13]. In this study, we prepared copper oxide thin film coating deposited on highly reflecting aluminium substrate using simple and environmentally sol-gel dip-coating, and investigated the surface electronic structure and the optical (absorptance and emittance) properties. The parameters studied are concentrations of copper nitrate concentrations and the dip-drying cycles whereby they were directly correlated to the thickness of the thin films which ultimately influences their solar absorptance.

2. EXPERIMENTAL

2.1. Preparation of thin film coatings

Copper (II) nitrate trihydrate ($Cu(NO_3)_2.3.H_2O$) (Merck), propionic acid (C_2H_5COOH) and absolute ethanol (Merck) were used as received. The cleaned

commercial aluminium size 2x4 cm^2 was used as substrate. Copper nitrate powder, coplexing agent propionic acid and absolute ethanol were mixed together and stirred for 2 hours to form a series of 0.1 M, 0.2 M and 0.3 M of copper nitrate sol precursors. The sol solutions were then used for thin film deposition on aluminium substrates via dip-coating at withdrawal rate of 180 mm/min and subsequently heated at 150°C for 1 minutes. Copper-cobalt thin films with varying thicknesses were prepared by repeating the dip-heating cycle before final annealing in oven at temperature 500 °C for 1 hour.

2.2. Characterisations

Solar absorptance was calculated based on the AM1.5 solar spectrum standard via hemispherical reflectance recorded from 300 to 2650 nm using UV-Vis-NIR Jasco V-670 double beam spectrophotometer with 60 mm integrating sphere. Infrared reflectance spectra in the wavelength area from 2.7 to 15.4 μm were obtained using a reflected-off type of Perkin Elmer Spectrum 100 FTIR spectrometer within the range from 500 to 4000 cm^{-1}. The coating surface was contacted on the diamond surface area and a pressure arm was positioned and locked at force of 80 N to maintain homogenous attachment onto the surface. The reflectance spectrum was obtained after four scans with resolution of 2 cm^{-1}. Background correction was performed before the collection of each spectrum.

3. RESULTS AND DISCUSSION

3.1. Absorptance properties

The absorptance (α) in the solar wavelength range of 0.3-2.5 μm is the most importance properties to measure the optical performance of material. Absorptance is defined as a weighted fraction between absorbed radiation and incoming radiation (I_{sol}) [14, 15]. The solar absorptance of a thin film on a substrate can be determined in term of reflectance as described by Duffie and Beckman [15] as seen in Equation (1). Low spectral reflectance indicates high absorptance and *vice versa*.
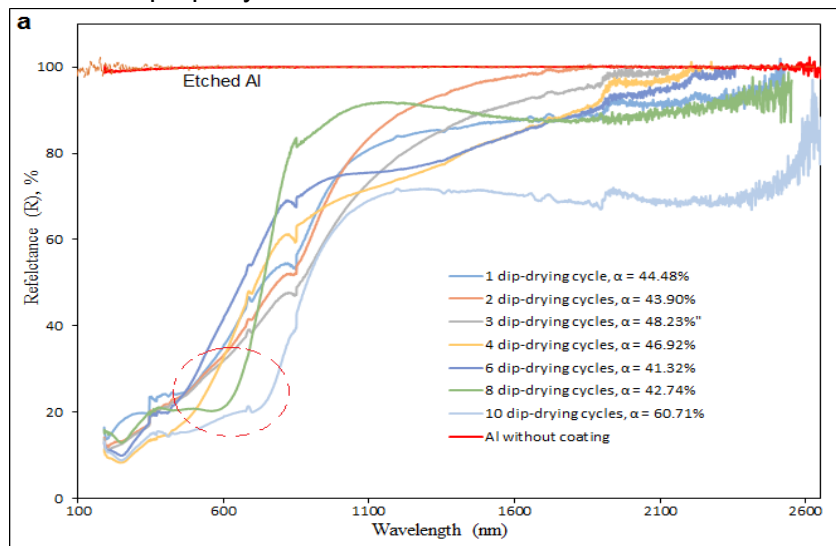
$$\alpha = \frac{\int_{0.3}^{2.5} I_{sol}(\lambda)(1 - R(\lambda))d\lambda}{\int_{0.3}^{2.5} I_{sol}(\lambda)d\lambda} \tag{1}$$

Reflectance spectra of the copper thin film coatings on aluminium substrates produced with variations of dip-drying cycle are shown in Fig. 1. Every spectrum has its corresponding solar absorptance values determined practically based on

the spectral distribution of terrestrial beam normal radiation at Air Mass (AM) 1.5 [15].

Generally the synthesized coatings have a low reflectance (< 50 %) in UV-Vis range, and moderate to high reflectance (up to 100 %) in near infrared range (NIR) (Fig. 1a-c). Such reflectance spectra approach a solar selective absorber (SSA) curve profile where they absorb much and moderate in UV-Vis and NIR wavelengths area, respectively. High absorption in UV-Vis area could be due to the existence of numeous spin-allowed electron transitions (octahedral arrangements) between partially filled d-orbitals [16, 17], while the moderate absorption in the NIR wavelength area is due to the combination effect between the absorber coating intrinsic properties and the aluminum substrate reflective properties. In this context our absorber coating behave akin a semiconductor. It is apparent that the stand alone aluminum substrate without coating has different spectra profile which reflects back almost all of solar radiations.

The reflectance property of substrate has a substantial influence on the overall

performane seletive absorber coating. It is well accepted that in the infrared area, the longer the radiation wavelength, the more radiation will be transmitted through the semiconductor coating material due to the smaller energy owned by the radiations/photons, which makes it easier for radiation to pass through the coating material without being absorbed. This transmitted-through radiation will be then reflected back by the reflective substrate (dark mirror
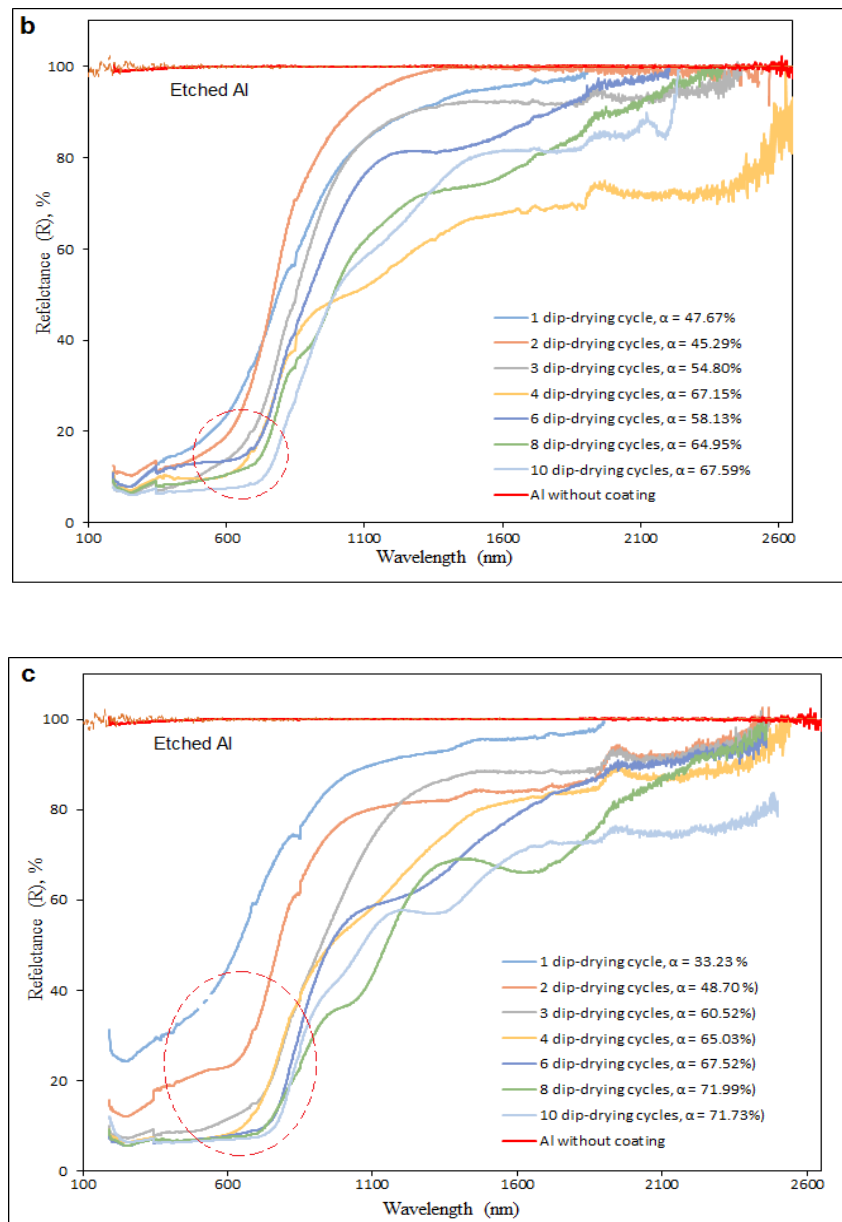
Fig. 1. Reflectance Spectra of Copper Oxide Thin Film Coatings on Aluminium Substrates Synthesized at Copper Nitrate Concentrations of: a) 0.1M, b) 0.2M, c) 0.3M with Corresponding Solar Absorptance (α) Values.

absorber–reflector tandem). In view of this, the more reflective surface properties, the more IR reflection and the better emittance will be.

In figure 1a-c, it can be seen that even though there are little fluctuations, generally the increase in the number of the dip-drying cycles (which increases the thickness of the film) improve the absorptance (α) value. It is well known that

the thickness of the absorber layer determines the final absorptance of the system [18, 19]. Similar phenomenon of absorptance improvement is also detected when the concentrations of sol precursor were increased. The highest absorptance (α=72%) is reached when the coating was synthesized using copper nitrate sol concentration of 0.3M deposited on aluminum substrate via 8 dip-drying cycles. It is estimated that the absorptance value wil be countinously increase until a certain higher sol precursor concentration and certain dip-drying cycles. However the optimum absorptance is limited by a criteria where the reflectance spectra and the cut-off line (at λ=2.5µm) are intersected at a absorptance value of minimum at least 50% [11].

An absorption adge is observed in every reflectance spectrum (red circle dashed line in figure 1a-c) which is formed due to the change of two reflectance slope when the wavelength is increased in wavelengths area below of 800 nm. It is clearly observed in figure 4b-c that generally the absorption edge moves to a longer wavelength when the dip-drying cycles are increased. When a high concentration of sol precursor was applied the increase of dip-drying cycles significantly increase the absorption edge position (Fig. 1c). However, overall, the absorption edges here in the positions of below 1000 nm which leads to relatively low absorptance compared other reports [11, 18]. It is impotant to note that the presence of absorption edge is normally begun by the presence of the interference peak as reported by other researches [10, 18, 20]. The presence of wavy curve (interference peak – absorption edge pair) is due to the combination factors of between the high refractive index of the absorber material and the and the low reflections in thi area. However, here, there is a minimum interference peaks observed, and it is a good sign for the improvement of the absorptance value when the high concentrations of copper sol concentration and high dip-drying cycles would be applied.

3.2 emittance properties

The emittance is the another properties to measure the performance of optical material. Thermal emittance (ε) is defined as a weighted fraction between the emitted radiation and the Planck black body distribution (*Ip*) and expressed in term of reflectance (*R(λ)*) as seen in the following equations [21]:

$$\varepsilon_{(T)} = \frac{\int_{2.5}^{20} I_P(\lambda)(1 - R(\lambda))d\lambda}{\int_{2.5}^{20} I_P(\lambda)d\lambda} \qquad (2)$$

The emittance vaule (ε) is practically determined based on the reflectance spectra using table of fraction of blackbody radiant energy between zero and λT for even increments of λT as described in Duffie and Beckman [15]. High spectral

reflectance indicates low thermal emittance/low heat loss from the surface and vice versa. The reflectance spectra of the copper oxide thin film coatings synthesized using 0.3 M copper sol precursor and 8 times dip-drying cycles (the coating with the best absorptance) within the infrared wavelength range is presented in Fig. 2. In Fig. 2, it can be seen that there are infrared weak absorption in wavelengths area of around 10 μm and 14.5 μm. They could be attributed to the phonon absorption typically exhibited by the copper or cobalt oxide family [22].

The processing of reflectance data via spreadsheet based on the Duffie Beckman method [15] results the emittance value of $\varepsilon=6.63\%$. This result is quite low for a slective absorber material since it is lower than 10% [23]. Based on this we can measure the selectivity of coating s = α/ε = 0.72/0.663 $\cong$ 1.1.
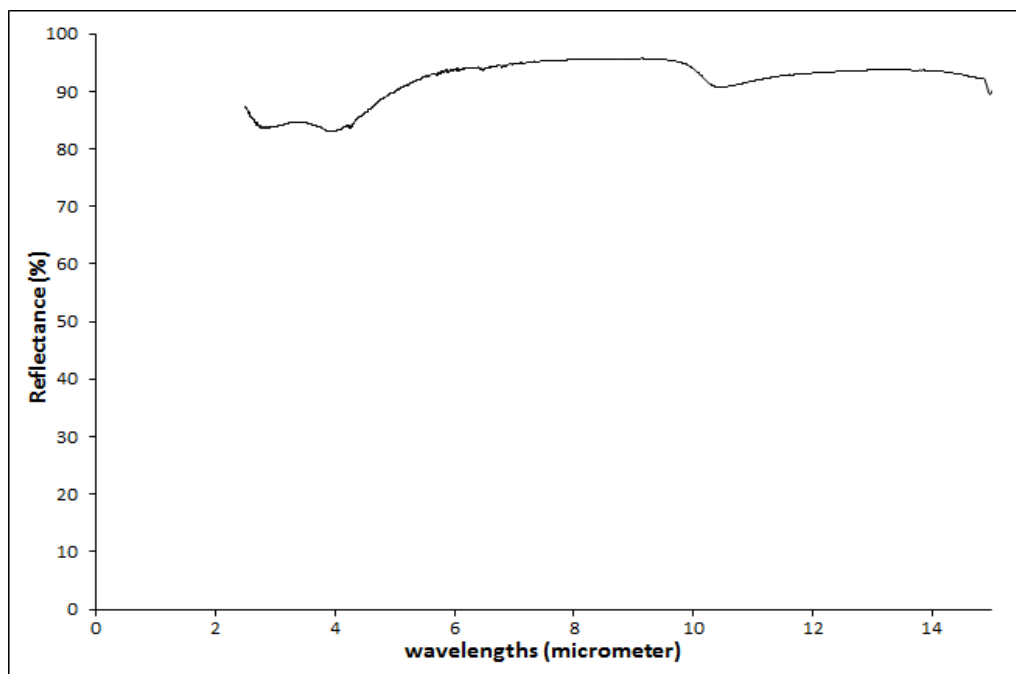
Fig. 2. Reflectance Spectra of Copper Oxide Thin Film Coatings on Aluminium Substrates Synthesized at Copper Nitrate Concentrations of 0.3M and 8 Times Dip-Drying Cycles.

4. CONCLUSIONS

Copper oxide thin film coatings have been successfully deposited on commercial highly reflective aluminium substrates using sol-gel dip-coating method. UV-Vis-NIR and FTIR reflectance spectra revealed that the increase in the number of the dip-drying cycles (which increases the thickness of the film) in the coating preparation improve the absorptance (α) value. Likewise with the

increase of the sol precursor concentration. The highest absorptance (α=72%) is reached when the coating was synthesized using copper nitrate sol concentration of 0.3M deposited on aluminum substrate via 8 dip-drying cycles. The emittance value of 6.63% for this coating was recorded.

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