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Solar absorptance of copper cobalt oxide thin film coatings with nanosize, grain-like morphology: Optimization and synchrotron radiation XPS studies

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Abstract

Copper-cobalt oxides thin films had been successfully coated on reflective aluminium substrates *via* a facile sol-gel dip-coating method for solar absorptance study. The optimum absorptance in the range of solar radiation is needed for further optimum design of this material for selective solar absorber application. Field emission scanning electron microscopy was used to characterize the surface morphology of the coating whereby nano-size, grain-like morphology was observed. Synchrotron radiation x-ray photoelectron spectroscopy was employed to analyze the electronic structure of the coated surface showing that the (i) oxygen consisted of lattice, surface and subsurface oxygen, (ii) copper consisted of octahedral and tetrahedral Cu⁺, as well as octahedral and paramagnetic Cu²⁺ oxidation states, and (iii) cobalt consisted of tetrahedral and paramagnetic Co(II), octahedral Co(III) as well as mixed Co(II,III) oxidation states. In order to optimize the solar absorptance of the coatings, relevant parameters such as concentrations of cobalt and copper, copper/cobalt concentration ratios and dip-speed were investigated. The optimal coating with $\alpha =$ 83.4% was produced using 0.25 M copper acetate and 0.25 M cobalt chloride (Cu/Co ratio = 1) with dip-speed 120 mm/min (four cycles). The operational simplicity of the dip-coating system indicated that it could be extended for coating of other mixed metal oxides as well.

Keywords: Sol-gel method; solar absorptance; copper-cobalt oxide; thin film coating; synchrotron radiation XPS

1. Introduction

Cobalt copper oxides $(Cu_x Co_y O_z)$ have attracted attention from many researchers worldwide for applications such as catalysis in oxygen evolutions reaction (EOR), Fischer-Tropsch process, synthesis of syngas-based alcohol, thermoelectricity material, etc. [1-12]. Many studies have been conducted to characterize the various properties of copper-cobalt oxides. De Koninck et al. [8] studied the physicochemical and electrochemical properties of Cu_xCo_{3-x}O₄ powder as applied for EOR. They found that CuCo₂O₄ particles had smaller crystalline structures (with crystallite size 10 times smaller) than Co_3O_4 . Furthermore, $CuCo_2O_4$ composite electrode that contained the largest amount of oxide particles had a high intrinsic electrocatalytic activity for the EOR. Volkova et al. [11] have used CuCoO₂ as precursor for Cu-Co alloy selective catalyst in the higher alcohol synthesis from syngas. They investigated the peculiarities of formation and destruction of Cu-Co alloy and Co₂C to understand their roles in higher alcohol synthesis. They found that the role of Cu-Co alloy consisted of formation of cobalt carbide was able to activate CO undissociatively that led to oxygenates synthesis. Beekman et al. [13] had characterized the delafossite-type CuCoO₂ prepared by ion exchange (metathesis) solid-state reaction between CuCl and LiCoO₂. They analyzed the electrical transport and magnetic susceptibility data for CuCoO₂. They found that transport and magnetic susceptibility data for polycrystalline CuCoO₂ were consistent with formal charge assignments of Cu⁺ and Co³⁺ for the transition metal constituents, and corroborated recent density functional theory calculations. Singh [12] studied the electronic and thermoelectric properties of CuCoO₂ by density functional calculations. Application of Boltzmann transport theory to the calculated band structure shows high thermopowers comparable to Na_xCoO₂, an established material for thermoelectric power generation application for both p- and n-type doping [12].

In order to harness the beneficial properties of such metal oxides, we had, therefore, conducted deposition of new cobalt-based metal oxide thin films ($M_x Co_y O_z$ with M = Mn, Cu, Ni) on commercial aluminum and glass substrates using sol–gel dip-coating method [14]. Our study revealed that $Cu_x Co_y O_z$ thin film coatings exhibited favourable optical properties, albeit it was clear that further optimization study would be required to facilitate commercialization of these coatings. To the best our knowledge, solar-based optical properties and optimization aspects of copper-cobalt oxides thin film coating are comparatively less studied [6] and as such, these features form the basis for the present study.

The objectives of the study were to optimize the solar absorptance of cobalt copper oxides thin films *via* dip-coating method. The parameters studied are concentrations of cobalt and copper, copper/cobalt concentration ratios and dip-speed whereby they are directly correlated to the thickness of the thin films which ultimately influences their solar absorptance. The film surface was characterized using field emission scanning electron microscopy (FESEM) and Synchrotron radiation x-ray photoelectron spectroscopy (SR-XPS).

2. Experimental

2.1. Preparation of thin film coatings

Preparation of the cobalt copper oxides thin film coatings was conducted as reported in our previous study [14]. Copper (II) acetate monohydrate (Cu(OOCCH₃)₂.H₂O, Alfa Aesar, 98 %), Cobalt (II) chloride (CoCl₂.6H₂O, APS Chemical, > 99 %), propionic acid (C₂H₅COOH, Chem Supply, 99 %) and absolute ethanol (Merck) were used as received. Substrate (size $2 \times 4 \text{ cm}^2$) used in this study was a highly reflective aluminium foil supplied by Anofol.

Copper acetate and cobalt chloride with varying concentrations (0.15 M, 0.2 M, 0.25 M; with Cu/Co molar ratio of 0.5, 1 and 2) were mixed using absolute ethanol. Propionate acid was subsequently added to the solution as a complexing agent and stirred for 2 hours. The resulting solution was used for thin film deposition on aluminium substrates *via* dip-coating method at withdrawal rate of 60 mm/min with relative humidity control under 55%. The samples were then heated on hot plate at 150°C for 10 seconds. Copper-cobalt thin films with distinct thicknesses were prepared by repeating the dip-heating cycle with different withdrawal rates before final annealing in an oven at 500 °C for 1 hour in air atmosphere and before allowed to cool to room temperature. The heating rate of the annealing process was 50°C/min.

2.2. Surface and solar absorptance analyses

Surface morphology of the thin film coatings was inspected using a FESEM (Zeiss Neon 40EsB). Sample was mounted on the substrate holder using carbon tape and sputter-coated with platinum to reduce charging effects prior to analysis. FESEM images were obtained using InLens detectors at various magnifications at 5 kV. Solar absorptance values were established using the AM1.5 solar spectrum standard *via* hemispherical reflectance recorded from 300 to 2700 nm *via* UV-Vis-NIR Jasco V-670 double beam spectrophotometer with 60 mm integrating sphere.

SR-XPS analyses were conducted on the soft X-ray beamline of the Australian Synchrotron under ring operation of 200 mA and 3 GeV. The beamline was equipped with a collimated light plane grating monochromator SX700. The 1200 lines/mm grating and 15 μ m entrance/exit slits were used. The samples were mounted on a stainless steel sample holder and characterized under a background pressure 10⁻¹⁰ Torr in the X-ray spectroscopy end-station. The Co 2*p*, Cu 2*p* and O 1*s* photoelectron lines were measured in XPS mode using photon energy of 1253.6 eV. The data were

processed using SPECS (V2.75-R25274) and CasaXPS (V.2.3.15) software. The photon energy scale was calibrated using C *1s* of saturated carbon (C-C/C–H) at 284.8 eV

3. Results and Discussion

3.1. Surface morphology

Fig. 1 shows the surface morphology of copper-cobalt oxide thin film coating (0.15 M copper acetate and 0.15 M cobalt chloride). The morphology of copper-cobalt coating indicates the presence of nano-sized grain-like particles with sizes ranging from 20 to 100 nm entrenched within jagged and uneven pores. Marsan *et al.* [7] and La Rosa-Toro *et al.* [15] reported similar porous structure for their produced copper-cobalt oxide ($Cu_xCo_{3-x}O_4$) layers. The former research group postulated that the porous/rough morphology of copper-cobalt oxide surface was attributed to the higher evolution of gas volumes (NO_2 , O_2) during the decomposition of concentrated nitrate coating. Concurrently, the porous/rough surface of fabricated copper-cobalt oxide coating is attributed to the evolution of O_2 from high temperature decomposition of copper and/or cobalt oxides which ultimately form a $Cu_xCo_yO_z$ system [16, 17].

3.2. Synchrotron radiation XPS study

A complementary high resolution synchrotron radiation X-ray Photoelectron Spectroscopy (SR-XPS) study affords detailed information on the electronic structure in the surface of the thin films. The synchrotron radiation source of XPS provides a continuous energy distribution over large energy region with high intensity and tuneability giving an optimal excitation energy instead of a fixed excitation energy source (either AlK_{α} or MgK_{α} radiation from a sealed-off X-ray tube) used in conventional XPS [18, 19]. The photon energies of synchrotron source can be varied to various

escape depth of out coming photon electrons and having a better photon ionization cross-section [20]. Furthermore, the beam size of the synchrotron light source is much smaller than the conventional photon sources, which helps to reduce the effects of the non-uniformity of the sample surfaces [20].

Fig. 2 shows the O *Is* SR-XPS spectra of copper cobalt oxide film coating synthesized using various concentrations. The O *Is* spectra exhibit a strong peak with a shoulder at a higher binding energy. The decoupling of the three O *Is* spectra generally gives four curve-fitting components in the spectrum from each sample. The peaks (labelled "i") at binding energy (BE) around 529.4-529.6 eV could be attributed to lattice O^{2-} (Cu-O, Co-O) [6, 8, 21], the peaks (denoted "ii") at BE around 530.5-530.8 eV may be treated as the surface oxygen from a wide variation of species such as adsorbed oxygen O⁻ and/or OH -like species, as hydroxyl, carbonate groups, *etc* [6, 8, 22-25], while the adjacent peaks (labelled "ii" and "iv") at BE around = 531.4-531.5 eV and at BE around 531.8-532.0 eV, respectively, could be assigned as subsurface O⁻ species [26, 27]. A relatively flat peak shoulder in the high energy side of O *Is* peak (Fig. 2.c) is due to the high percentage of surface oxygen and the low percentage of subsurface oxygen in the coating surface synthesized using a higher concentration of copper and cobalt precursors.

Fig. 3 shows the Cu 2p spectra and the peak-fitting of their Cu $2p_{3/2}$ of copper cobalt oxide film coatings synthesized using various concentrations. The two main peaks as Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks and the satellites on the high energy side of each Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively, are found in every spectrum (Fig. 3.a). The binding energy difference between Cu $2p_{1/2}$ and Cu $2p_{3/2}$ peaks in every sample which is around 19.8 eV indicated the presence a low oxidation states of copper, while the satellite peak between Cu $2p_{3/2}$ and Cu $2p_{1/2}$ confirm the presence of Cu²⁺ ions. The decoupling of Cu $2p_{3/2}$ and its satellite in every coating gives five curve-fitting components (Fig. 3. b-d) and the quantification analysis are presented in Table 1. It is commonly recognized that the Cu $2p_{3/2}$ photoelectron peak around of 933.3-934.0 eV with shake-up satellite is due to the CuO (or Cu^{2+}), while many researchers identified that the Cu $2p_{3/2}$ photoelectron peak at around of 932.5-932.8 eV is from the tetrahedral Cu⁺ with its counterpart peak from octahedral Cu⁺ located below the tetrahedral one [15, 28-36]. From Table 1, the octahedral and tetrahedral Cu⁺ as well as the octahedral and paramagnetic Cu^{2+} oxidation states are detected with the tetrahedral Cu^{+} being the most prominent. These results are relatively different from the copper acetate precursor used which has the Cu^{2+} oxidation state only. It is widely known that the increase in temperature changes the characteristic of oxidation states of a surface. In relatively low temperatures (under 150°C), the copper oxide obtained from alcohothermal process of copper acetate precursor undergoes a binding energy shifting of Cu²⁺ oxidation state from A-sites (tetrahedral coordination) toward to B-sites (octahedral coordination) as temperatures are increased [33, 37]. However, in this temperatures range, no reduction of Cu²⁺ occurred [37]. In copper cobalt oxides environment, the reduction of Cu²⁺ to Cu⁺ is detected at temperature of 350°C [15, 38]. The tetrahedral Cu⁺ species is strongly suspected from reduction of Cu²⁺ at tetrahedral sites [15]. In regard to the copper-cobalt oxide surface samples, the presence of oxidation states of copper with different coordinations is originally estimated from the evolution of Cu²⁺ A-sites due to decomposition/deligandation during the hightemperature (500°C) calcination. In addition, the low intensities of paramagnetic satellites of cupric oxide (Fig. 3a) indicate that a part of octahedral Cu²⁺ undergoes a further reduction forming the octahedral Cu⁺ [33, 39].

A quite broad and asymmetric of line shapes core-level main peaks profile (Fig. 4a) and the presence of cuprous (Cu^+) in the copper-cobalt oxide environment have been widely recognized as typical of monophasic Cu-Co mixed oxides [15]. In Cu-Co mixed oxides, the Cu^{2+} ions incorporate

into the surface octahedral vacancy and then could share oxygen with adjacent Co^{2+} ions which the Cu^{2+} ions are filling interstitial sites within the structure of the cobalt oxide forming surface Cu–O–Co species [15, 40].

Fig. 4 shows the Co 2p spectra and the decoupling of their Co $2p_{3/2}$ of copper cobalt oxide film coatings synthesized using various concentrations. The two main peaks were assigned as Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks and a low intensity satellite between these two main peaks were found in every spectrum (Fig. 4.a). Qualitatively the Co $2p_{3/2}$ peak and Co $2p_{1/2}$ peak separated by a spin-orbit splitting of around 15.1 eV indicate the presence the mixed Co(II) and Co(III), while the low intensity satellite of the Co 2p spectra in area of around 789 (Fig. 4a) on the copper-cobalt oxide surface system indicated that the cobalt ions are present in a partial spinel-type lattice arrangement. The observed asymmetry in the Co $2p_{1/2}$ peak confirms the existence of Co(II) and Co(III) ions. The curve-fitting of Co $2p_{3/2}$ and its satellites from every coating gives five peaks components (Fig. 4. bd). The peaks in the region of 779.1-780.0 eV are mostly due to Co₂O₃ (or Co(III)) and Co₃O₄ (or mixed Co(II,III)) bonding states. The peak binding energy of Co 2p_{3/2} above 780.0 eV with a shakeup satellite is characteristic of CoO (or Co(II)). In copper-cobalt oxide environment, the types of coordination (octahedral/tetrahedral) of Co $2p_{3/2}$ have been specifically identified by some researchers [6, 8, 40]. The quantitative analysis of Co $2p_{3/2}$ is presented in Table 2. From Table 2, the tetrahedral and paramagnetic Co(II), octahedral Co(III) as well as mixed Co(II,III) oxidation states are detected with the tetrahedral Co(II) ions are predominant.

The presence of oxidation states here is quite different from the oxidation state of cobalt chloride precursor used. The cobalt chloride has been widely known to contain the octahedral cobalt(II) oxidation state surrounded by six chloride ions. The changes in oxidation state due to the thermal influence on the cobalt oxide surface synthesized from cobalt chloride precursor are needed to

understand our results. In a relatively low temperature synthesis process (under 100 °C), the cobalt oxide surface synthesized using cobalt chloride precursor has already shown a differentiation in the oxidation states composition by the presence of both Co(II) and Co(III) species [41]. In a higher temperatures treatment of around 330-350 °C, the mixed oxidation states of cobalt (Co₃O₄) which has a normal spinel crystal structure based on a close-packed face centered cubic configuration of O²⁻ ions where Co(II) ions occupy the one-eighth of the tetrahedral A-sites and Co(III) ions occupy one-half of the octahedral B sites are detected [42]. Further, the octahedral Co(III) ions here have a more significant role determining the surface activity rather than tetrahedral Co(II) [42, 43]. The relative amount of Co(II) ions in tetrahedral sites is found to increase with the increase of calcination temperature from 450-650°C [44] due to the reduction of Co(III). Finally, it is widely known that at around 950 °C, the mixed Cobalt(II,III) oxidation states convert fully to cobalt(II) oxide with the following reaction: $2 \text{ Co}_3\text{O}_4 \rightarrow 6 \text{ CoO} + \text{O}_2$. In line with this evolution, it can be understood that the presence of various cobalt oxidation states corresponds with different types of coordination in our samples, and the tetrahedral Co(II) ions are the predominant one since the temperature synthesis is above 450 °C.

In a copper-cobalt mixed oxides system, the Co(II) ions are partially substituted by Cu^{2+} ions [8, 45]. If Cu^{2+} ions and octahedral Co(III) ions are present in the copper-cobalt oxide system, then the oxide could be represented by the $Cu^{2+}Co_2^{III}O_4$, a form of copper-cobalt spinel structure.

3.3. Solar absorptance

The solar absoprtance (α) values of the synthesized copper-cobalt thin film coatings were determined based on reflectance (R) as described by Duffie and Beckman [46]. Low spectral reflectance essentially implies high absorptance and *vice versa*. An important point is that the

thickness of the absorber coating layer influences the final absorptance of the system [47-49]. In the case of dip-coating, film thickness can be easily controlled and optimized by altering the dip-drying/heating cycles or the withdrawal rate [50]. As such, the dip-heating process was conducted at several pre-fixed cycles. Fig. 5 shows the reflectance spectra of copper-cobalt oxide thin film coatings on aluminium substrates with equimolar copper and cobalt concentrations of 0.15, 0.2, 0.25 and 0.3 M, respectively. Four dip-heating cycles were selected since they basically afford an optimized reflective system compared to other number of cycles (results not shown for other cycles for the reason of brevity).

Interestingly, a wavy curve with peak (interference peak) and valley (absorption edge) was detected at the shorter wavelengths range of spectra. A similar phenomenon was also reported by other researchers [47, 51]. Generally, the interference peak and the absorption edge shift towards to longer wavelengths when increasing the dip-speed and concentrations. On the other hand, the amplitude of the wavy curves oscillation tends to decrease with an increase in the concentrations of metal ions. The absorptance values are higher for faster dip-speeds or higher concentrations. Nonetheless, in order to obtain optimized spectra with selective solar absorption, the position of reflectance value in the cut-off area (wavelength at around 2500 nm) has to be relatively high, i.e. at least 50% of the reflectance value. The film coating synthesized using concentrations of 0.25 M copper acetate and 0.25 M cobalt chloride (Cu/Co ratio = 1) with dip-speed 120 mm/min (Fig. 5c, α = 83.4%) can be construed as the optimum coating design in our study.

In addition, we have examined the relative effect of concentration ratios on the reflectance of copper-cobalt oxide thin film coatings. The Cu/Co concentration ratios investigated are 0.5 (0.125 M copper and 0.25 M cobalt), 1 (0.25 M copper and 0.25 M cobalt) and 2 (0.25 copper and 0.125 M cobalt), respectively. The dip-speed is 120 mm/min with four dip-heating cycles. It shows that the

positions of the interference peaks and the absorption edges shift towards the longer wavelengths as the Cu/Co ratio is decreased (Fig. 6). The absorption edge of the film coated with Cu/Co ratio = 0.5reaches a reasonably long wavelength at ca 1500 nm with lower interference peak and absorption edge than the spectrum for Cu/Co ratio = 1. These render the absorptance value of the film coating with Cu/Co = 0.5 the highest among the three spectra, at about 86.77%. However, even though its reflectance position in the cut-off area is relatively lower than the coating with Cu/Co ratio = 1, the curve profile of film coating synthesized with Cu/Co ratio = 0.5 can be considered as optimum since the latter exhibits higher absorptance value. The absorptance value of 86.77% appears to be comparatively promising for the application of selective absorber systems (i.e. before the addition of anti-reflective layer). By comparison, other reported coatings synthesized using complicated solgel method exhibited absorptance values of $\alpha = 83 \%$ [47], 80-85 % [52] and 80 % [53]. We surmise that the nano-sized grain-like particles surrounded by pores-trenches in our samples are capable of providing a conducive surface morphology for absorption of incidental solar radiation due to the multiple reflections that can occur inside the pore/aggregate [54]. As such, this boosts the absorptance due to the interaction and relaxation mechanism in absorber as well as multiple reflections and resonant scattering in the pore [54, 55]. At the same time, the highly reflective aluminium substrate functions to reflect back the lower energy radiation (infra-red) that penetrates the film coating.

4. Conclusions

In this study, copper-cobalt oxides thin film coatings had been successfully deposited on highly reflective aluminium substrates using a sol-gel dip-coating method. The surface of the coating exhibited grainy morphology at nano scales. SR-XPS showed that (i) the oxygen consist of lattice,

surface and subsurface oxygen, (ii) copper consist of octahedral and tetrahedral Cu⁺, octahedral and paramagnetic Cu²⁺ oxidation states, and (iii) cobalt consist of tetrahedral and paramagnetic Co(II), octahedral Co(III) as well as mixed Co(II,III) oxidation states. Absorptance optimization study revealed that the coating synthesized using 0.25 M copper and 0.25 M cobalt (Cu/Co ratio = 1) with dip-speed 120 mm/min (four cycles) represented the optimal coating design with α = 83.4%. The simplicity of the dip-coating system which facilitated the sol-gel process implied that such system could be extended for coating of other mixed metal oxides as well. Our data can be used to aid the engineering design of highly tuneable thin film metal oxides for numerous industrial applications.

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Figure captions

Fig. 1. FESEM micrographs of the copper-cobalt oxide thin film coating (0.15 M copper acetate and 0.15 M cobalt chloride).

Fig. 2. O *1s* SR-XPS spectra of copper cobalt thin film coatings synthesized using concentrations of a) 0.15 M copper and 0.15 M cobalt, b) 0.2 M copper and 0.2 M cobalt, and c) 0.25 M copper and 0.25 M cobalt.

Fig. 3. a) Cu 2p SR-XPS spectra of copper cobalt thin film coatings synthesized using various concentrations, b-d) decoupling of Cu $2p_{3/2}$ of copper cobalt thin film coatings synthesized using various concentrations

Fig. 4. a) Co 2p SR-XPS spectra of copper cobalt thin film coatings synthesized using various concentrations, b-d) decoupling of Co $2p_{3/2}$ of copper cobalt thin film coatings synthesized using various concentrations

Fig. 5. Reflectance spectra of copper-cobalt oxide thin film coatings on aluminium substrates. Concentrations of reactants: a) 0.15 M copper and 0.15 M cobalt; b) 0.2 M copper and 0.2 M cobalt; c) 0.25 M copper and 0.25 M cobalt; d) 0.3 M copper and 0.3 M cobalt. Four dip-heating cycles were carried out.

Fig. 6. Effect of Cu/Co concentration ratios on the reflectance of copper-cobalt oxide thin film coatings. These include Cu/Co concentration ratios of 0.5 (0.125 M copper and 0.25 M cobalt), 1 (0.25 M copper and 0.25 M cobalt) and 2 (0.25 copper and 0.125 M cobalt), respectively. The dipspeed is 120 mm/min with four dip-heating cycles.

Table 1. The decoupling of Cu $2p_{3/2}$ and its satellites of copper cobalt film coatings synthesized using various concentrations.

| Coatings synthesized | Binding ener | rgy and the perce of Cu $2p_{3/2}$ photo | Binding energy and the percentage of satelites | | |
|-------------------------|----------------------------|---|--|------------------------------|------------------------------|
| concentrations | | | | | |
| Label | i | ii | iii | Sat. I | Sat. II |
| [Cu]=[Co]=0.15M | 931.2 eV (3.8 | 932.8 eV (53.7 | 933.8 eV (31.9 | 940.7 eV (5.6 | 943.2 eV (5 |
| | at%) | at%) | at%) | at%) | at%) |
| [Cu]=[Co]=0.2M | 931.2 eV (2.9 | 932.7 eV (48.7 | 933.7 eV (35.4 | 941.3 eV (10.6 | 943.8 eV (2.4 |
| | at%) | at%) | at%) | at%) | at%) |
| [Cu]=[Co]=0.25M | 931.4 eV (4.9 | 932.8eV (56 | 933.6 eV (32.1 | 940.5 eV (3.1 | 943.2 eV (3.8 |
| | at%) | at%) | at%) | at%) | at%) |
| Attributations | Octahedral Cu ⁺ | Tetrahedral Cu ⁺ | Octahedral Cu ²⁺ | Paramagnetic | Paramagnetic |
| | [33-36] | [15, 28-32] | [8, 15, 39, 40, | Cu ²⁺ [8, 15, 28, | Cu ²⁺ [8, 15, 28, |
| | | | 56-58] | 38, 57, 59] | 38, 57, 59] |

Table 2. The Co $2p_{3/2}$ and its satellite curve-fitting of copper cobalt film coatings synthesized using various concentrations.

| Coatings synthesized using | Binding ener components c | gy and the perce of Co $2p_{3/2}$ photo | Binding energy and the percentage of satellites | | |
|----------------------------------|------------------------------|--|---|----------------|----------------|
| Label | i | ii | iii | Sat I | Sat II |
| Lucci | Ĩ | 11 | | Sut. I | Sut II |
| [Cu]=[Co]= 0.15M | 779.2 eV (11.5 | 779.8 eV (25 | 780.8eV (48.4 | 785.6eV (9.2 | 789.1eV (5.9 |
| | at%) | at%) | at%) | at%) | at%) |
| [Cu]=[Co]= 0.2M | 779.1 eV (17.15 | 779.9 eV (23.7 | 780.9eV (45.5 | 785.6eV(8.3 | 788.9eV (5.3 |
| | at%) | at%) | at%) | at%) | at%) |
| [Cu]=[Co]= 0.25M | 779.4 eV (11.8 | 780 eV (30.4 | 781 eV (46.4 | 786 eV (5.9 | 789 eV (5.4 |
| | at%) | at%) | at%) | at%) | at%) |
| Attributations | Octahedral | Co(II,III) [40, | Tetrahedral | Paramagnetic | Paramagnetic |
| | Co(III) [6, 8, 22, | 44, 45, 60] | Co(II) [8, 39, | Co(II) [8, 43] | Co(II) [8, 43] |
| | 43] | | 40, 43] | | |



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Fig. 4. a) Co 2p SR-XPS spectra of copper cobalt thin film coatings synthesized using various concentrations, b-d) decoupling of Co $2p_{3/2}$ of copper cobalt thin film coatings synthesized using various concentrations



Fig. 5. Reflectance spectra of copper-cobalt oxide thin film coatings on aluminium substrates. Concentrations of reactants: a) 0.15 M copper and 0.15 M cobalt; b) 0.2 M copper and 0.2 M cobalt; c) 0.25 M copper and 0.25 M cobalt; d) 0.3 M copper and 0.3 M cobalt. Four dip-heating cycles were carried out.



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