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1 **Structural Thermal Stability of Graphene Oxide-doped Copper-cobalt Oxide**
2 **Coatings as a Solar Selective Surface**

3

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27
28 3d transition metal oxides based thin film coatings such as copper-cobalt oxides exhibit high
29 absorption in the visible region and low emittance in the infra-red to far-infra-red region of the
30 solar spectrum which is favourable for use as potential selective surface materials in
31 photothermal devices. These materials have the potential to minimize heating while increasing
32 absorption in the operative spectrum range and therefore achieve higher solar selectivity. A
33 series of mixed copper-cobalt metal spinel oxides ($\text{Cu}_x\text{Co}_y\text{O}_z$) doped with graphene oxide thin
34 films were deposited on commercial grade aluminium substrates using a sol-gel dip-coating
35 technique at an annealing temperature of 500 °C in air for 1 h. Characterizations of the
36 synthesized films were carried out by high temperature synchrotron radiation X-ray Diffraction
37 (SR-XRD), UV-Vis, Fourier Transform infrared spectroscopy (FTIR) and X-ray photoelectron
38 microscopy (XPS) techniques. High thermal stability of coatings with multiple phases, binary
39 and ternary metal oxides, was defined through SR-XRD study. FTIR analysis shows moderate
40 (<80%) to high (up to 99%) reflectance in the infra-red region while the UV-Vis investigations
41 demonstrate that, in the visible region, solar absorption increases gradually (up to 95%) with the
42 addition of graphene oxide to the $\text{Cu}_x\text{Co}_y\text{O}_z$ coatings. With the incorporation of 1.5 wt% of
43 graphene oxide to the copper-cobalt oxide coatings, a high solar selectivity of 29.01 (the ratio of
44 the average solar absorptance in visible and the average thermal emittance in infra-red to far
45 infra-red region; α/ε) was achieved.

46
47 **Key words:** Coatings; Sol-gel method; Surface bonding; Thermal stability; Synchrotron
48 radiation; Fourier transform infrared spectroscopy; X-ray diffraction; X-ray photoelectron
49 spectroscopy

50

51

52 **1. Introduction**

53 Over the years, cobalt based mixed metal oxide thin films have been extensively studied
54 by different groups around the world owing to their wide-spread applications^[1-4]. Pure copper
55 oxide^[5], cobalt-copper oxide, manganese-cobalt oxide, nickel-cobalt oxide^[6,7], and copper-
56 aluminium oxide^[8] have been used as high performance optical selector or absorbers. The
57 physicochemical and electrochemical properties of $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ powder has been investigated for
58 their practical applications as catalysts in oxygen evolutions reactions (EOR)^[9]. There have been
59 numerous investigations of mixed metal oxide thin films pursuing improved physicochemical,
60 optical, thermal, electro-chemical, photo-chemical, magnetic, dielectric and electro-magnetic
61 properties focusing on their potential practical applications in the areas such as clean energy
62 devices, solar cells, photovoltaics, thermal collectors, solar selective absorbers, and smart
63 windows. Optical characterizations, thermal durability studies, physicochemical and mechanical
64 properties of sol-gel derived Cu-Co oxide coatings have been investigated by other groups^[10,11].
65 In a recent study, Rahman et al.^[12] reported the annealing temperature effects on the
66 morphological, mechanical, solar selective characteristics and local electronic bonding states of
67 metal nitride based thin film coatings. Synthesis mechanisms, cyclic stability and
68 electrochemical performance of graphene-carbon nanotube hybrid films, graphene based

69 metal/metal oxides nanocomposite and nano-sized Co_3O_4 materials have been extensively
70 discussed in earlier studies^[13–15].

71 Optical applications of graphene oxide is also well-known^[16]. The high optical absorption
72 and tuneable optical band-gap are the most appealing characteristics of graphene that make it an
73 ideal material for the effective light harnessing^[17]. Light absorbing photovoltaic applications of
74 graphene based materials have been reported in an earlier study^[18]. Optical absorption and power
75 conversion efficiency of layer-transferred graphene in organic hybrid solar cells have been
76 reported^[19]. The application of graphene in organic photovoltaic devices has been reported by
77 Arco *et al.*^[20] and Liu *et al.*^[21]. Graphene has been reported to be a promising candidate for
78 offering improved efficiency of light harvesting devices e.g., inorganic, organic^[23,24], hybrid^[25],
79 and dye sensitized solar cells^[26]. A series of comprehensive reviews focused on investigating
80 manufacturing aspects, properties, and applications of graphene and graphene-based materials in
81 energy related areas^[27–29]. Optimization of optical properties of inorganic compounds mixing
82 with graphene oxide forming a hybrid system is also feasible in the development of graphene
83 oxide-based selective surface. As graphene oxide offers good solubility in aqueous and polar
84 solvents, the sol-gel method is a feasible technique to prepare graphene oxide based thin films.
85 These coatings exhibit high transmittance and the strong ability to resist abrasion, which make
86 them suitable for applications in some harsh conditions.

87 In the past few years, numerous strategies have been adopted in the design of metal oxide
88 based light harvesting assemblies. For instance, sol-gel derived mixed metal oxides based thin
89 film selective solar surfaces attracted attention due to their flexibility and advantages e.g., cost-
90 effective, good thermal and physicochemical stability, easy preparation process, shorter
91 processing time, low-toxicity, less equipment needed, tuneable electronic band gap, and high

92 electron mobility. Despite the availability of numerous literature on metal oxide thin films and
93 graphene oxide thin films for their optical and light harvesting purposes, however, to the best of
94 our knowledge, utilization of mixed metal oxide with graphene oxide thin films as solar selective
95 surface is yet to be explored. Nowadays, synchrotron radiation has emerged as a powerful and
96 versatile analytical tool for materials production (*e.g.*, fabrication of microelectronic devices),
97 quality control, and materials evaluation in industrial research and development. Synchrotron
98 radiation possesses some salient features; very high intensity, high brightness, good stability,
99 higher degree of polarization, wide energy range extending from infrared to X-ray wavelengths
100 and so on. In synchrotron radiation, many different beamlines are involved and each beamline is
101 designed for a specific type of research. For different beamlines, various techniques such as X-
102 ray absorption, scattering, diffraction, and fluorescence analysis are available for synchrotron
103 research. Synchrotron radiation facilities demonstrate superior capabilities to characterise various
104 properties of materials. A wide range of experiments such as structure resolutions, variable
105 temperature studies, structural studies of microporous materials, structure and property
106 investigations of solid metal oxides, phase identification and quantification of pharmaceuticals
107 ~~etc~~ can be successfully conducted at the synchrotron radiation-based powder diffraction (PD)
108 beamline's primary end station. Synchrotron radiation-based spectroscopy is also used to
109 investigate semiconductor and thin film surfaces to realize the interface formation among the
110 constituents. Furthermore, the synchrotron radiation core level emission spectra, the chemical
111 composition of the surface of the films, and the detection of the surface core level components
112 can be used to explain the bonding configurations of the thin film coatings. The synchrotron
113 radiation based spectroscopy thus assists revealing the interface formation and new development
114 and applications can be evolved. For example, synchrotron radiation based near-edge X-ray

115 absorption fine structure (NEXAFS) initiated by the electron transfer from a core orbital to
116 discrete or quasi-discrete unoccupied levels provide us with valuable information pertinent to the
117 electronic structures and local atomic structures. The local bonding structures around a specific
118 atom such as the coordination number, the bonding length, and the distribution of defects can be
119 estimated by analysing the peak positions of synchrotron radiation based experiments. In a recent
120 work^[30], we conducted NEXAFS experiments to sol-gel derived copper-cobalt oxide coatings by
121 measuring the $\text{Cu}L_{2,3}$ -edges, $\text{Co}L_{2,3}$ -edges and O K -edges. Our study demonstrated that the local
122 environments of Cu, Co and O remained invariant with the change in the copper to cobalt
123 concentration ratios except for the $[\text{Cu}]/[\text{Co}] = 2$ sample whereas the local coordination appeared
124 to slightly change due to the loss of octahedral Cu^+ . The $\text{Cu}-L_3$ and $\text{Cu}-L_2$ absorption edges
125 arisen from the dipole transitions of the $\text{Cu}2p_{1/2}$ for L_2 and $\text{Cu}2p_{3/2}$ for L_3 into the empty d states
126 while the $\text{Co}-L_3$ and $\text{Co}-L_2$ absorption edges appeared from Coulomb interactions and exchange
127 interactions of $2p$ core holes with the $3d$ electrons. The hybridization of the $\text{Co}3d$ states with
128 $\text{O}2p$ states and $\text{O}2p$ states with $\text{Co}4sp$ states and $\text{O}2p$ states was extended to a Co higher orbital
129 that was seen in the O K -edge NEXAFS peaks of copper-cobalt oxide coatings. In this study, we
130 attempt to develop the graphene oxide as a mixture into the $\text{Cu}_x\text{Co}_y\text{O}_z$ systems for the
131 development of the thin film based light harvesting devices with improved spectral selectivity.
132 We focus on the structural thermal stability and optical effects of graphene oxide modified
133 $\text{Cu}_x\text{Co}_y\text{O}_z$ composites in order to achieve better solar selective performance of coatings
134 fabricated via dip-coating sol-gel technology.

135

136 2. Experimental Methods

137 2.1. Sample preparation methodology

138 Cobalt (II) chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, APS Chemical, >99%), copper (II) acetate
139 monohydrate ($\text{Cu}(\text{OOCCH}_3)_2 \cdot \text{H}_2\text{O}$, Alfa Aesar, >98%), propionic acid ($\text{C}_2\text{H}_5\text{COOH}$, Chem
140 Supply, >99%), graphene oxide (concentration 1 mg/cc), and absolute ethanol (E. Mark of
141 Germany, >99%.) were used to make the sols for synthesizing thin films. The highly-reflective
142 commercial aluminium material (Anofol, size 2 cm \times 4 cm) was used as substrate for the
143 deposition of the coatings. The substrates were cleaned using a hot etching aqueous solution (85
144 $^\circ\text{C}$) prepared by mixing chromium (VI) oxide and phosphoric acid for 10 min in order to remove
145 the alumina layer. Substrates then were rinsed in hot mili-Q water followed by a flush of cooled
146 mili-Q water and dried in a flow of high purity nitrogen gas.

147 In preparing the sols, cobalt (II) chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.25 mol/L), graphene oxide, and
148 copper (II) acetate monohydrate ($\text{Cu}(\text{OOCCH}_3)_2 \cdot \text{H}_2\text{O}$) were mixed with absolute ethanol.
149 Propionic acid ($\text{C}_2\text{H}_5\text{COOH}$) was used as the complexing agent to the solution. After stirring the
150 mixed solution for 2 h, the resultant solution was used for thin film deposition on aluminium
151 substrates using a dip-coating technique. The dip and withdrawal rate were 180 mm/min and 60
152 mm/min, respectively. The sample coating was heated at 150 $^\circ\text{C}$ for 60 s. A relative humidity of
153 50% was maintained during the entire period of the coatings preparation process. The same dip
154 coating process, using same sol solution, was repeated four times to increase the thickness of
155 film with better uniformity. Finally, the samples were annealed at 500 $^\circ\text{C}$ in air for 1 h. The
156 heating rate of the furnace for annealing was kept at 50 $^\circ\text{C}/\text{min}$ and the samples were left in the
157 furnace for 10 min after power was turned off.

158

159 *2.2. Characterizations of thin film coatings*

160 High resolution synchrotron radiation X-ray diffraction (SR-XRD) measurements of the
161 $\text{Cu}_x\text{Co}_y\text{O}_z$ coatings with and without graphene oxide were conducted using the powder
162 diffraction (PD) beamline 10-BM-1 at the Australian synchrotron, Melbourne. The PD beamline
163 at Australian Synchrotron utilises a bending magnet source. The beamline was operated at 2.5
164 GeV which produces a continuous spectrum of photons in the range 5–30 keV with a maximum
165 flux of about 10^{13} photons/s at an angular acceptance of 0.23 mrad vertical by 2.5 mrad
166 horizontal. The samples were loaded in 0.3 mm diameter quartz capillaries with diamond
167 powders that are rotated during the measurements. A MYTHEN II microstrip detector system
168 was used in a $2\theta = 18^\circ$ to 44° geometry in steps of 0.002° for 5 min at each detector settings for
169 SR-XRD data acquisition. The MYTHEN detector consists of 16 position sensitive detectors
170 keeping a 0.2° gap between detector modules. X-rays of wavelength $\lambda = 0.11267$ nm as
171 estimated with a LaB6 standard NIST 660a standard were used for SR-XRD measurements at a
172 beam size of 7 mm in width and 1 mm in height with an exposure time of 145 min. High
173 temperature measurements were achieved using an Anton Parr HTK20 furnace. The real time
174 temperature was monitored by a thermocouple in direct contact with the bottom substrate of the
175 coatings close to the irradiated area. The temperature difference between the top of the coating
176 and the bottom of the substrate was calibrated before XRD measurement. The heating and
177 cooling were remotely controlled via a computer interface. The acquired data were processed by
178 using the PDViPeR software in order to obtain the XRD patterns as presented in Figs. 1 and 2.

179 Chemical analysis of the outermost 5–10 nm atomic layers of the thin film coatings was
180 performed via the XPS technique. The Kratos Axis-Ultra photoelectron spectrometer uses Al $K\alpha$
181 monochromatic X-ray source with beam energy of 1486.6 eV at a power of ~ 10 mA and ~ 15 kV.
182 Square size samples (2 mm \times 2 mm) were mounted on steel sample holder. The pressure of the

183 XPS analyser chamber was maintained at 2.9×10^{-9} Torr. The $\text{Cu}2p$, $\text{Co}2p$, $\text{O}1s$, $\text{C}1s$
 184 photoelectron lines were recorded with a 2D delay line detector. The photoelectron energy scale
 185 was calibrated using $\text{C}1s$ (hydrocarbon; C–H) line-at 284.6 eV. CASA-XPS (Version 2.3.15)
 186 software was employed for data processing and curve fitting in order to define the component of
 187 photoelectron lines.

188 The photon energy dependence of absorption coefficient helps to study the band structure
 189 and the type of electron transition involved in absorption process. In crystalline and amorphous
 190 materials the photon absorption obeys the Tauc relation^[31–34],

$$191 \quad \alpha h\nu = A(h\nu - E_g)^n \quad (1)$$

192 where, α is the absorption coefficient, $h\nu$ is the incident photon energy, A is an energy
 193 independent constant, E_g is the band-gap energy and n is an index depending on the type of
 194 optical transition involved in photon absorption. The index $n = 1/2$ and 2 for direct and indirect
 195 allowed transitions and $n = 3/2$ and 3 for direct and indirect forbidden transitions, respectively^[32].
 196 Thus, the direct transition energy gap (direct band-gap energy) can be obtained by plotting $h\nu$ vs
 197 $(\alpha h\nu)^2$ and extrapolating the linear portion of the curve to $(\alpha h\nu)^2 = 0$ in the energy axis. Similarly
 198 the indirect energy band-gap can be found by plotting $h\nu$ vs $(\alpha h\nu)^{1/2}$ and extrapolating the linear
 199 portion of the curve to $(\alpha h\nu)^{1/2} = 0$ in the X -axis.

200 Solar absorbance of the coatings was determined using a double-beam UV–Vis
 201 spectrophotometer (Model: UV-670 UV-Vis spectrophotometer, JASCO, USA) with a unique,
 202 single monochromator design covering a wavelength range from 190 to 2200 nm. The
 203 monochromator consists of a 1200 grooves/mm grating and a photo multiplier tube (PMT)

204 detector for the UV-Vis measurements. The solar reflectance of the thin film coatings were
 205 measured using a FTIR spectrometer (Perkin Elmer Spectrum 100 FTIR Spectrometer, USA) in
 206 the wavelength of 2.5 to 15.5 μm . The solar absorptance and the thermal emittance of a material
 207 can be calculated from measurements of reflectance data from the-visible and infrared ranges of
 208 the solar spectrum^[35]. For a range of solar wavelengths, the total solar absorptance, α is defined
 209 as a weighted fraction between absorbed radiation and incoming solar radiation (I_{sol}), while
 210 thermal emittance, ε is defined as a weighted fraction between emitted radiation and the Planck
 211 black-body distribution (I_p) and can be computed using Eqs. (2) and (3)^[35]:

$$212 \quad \alpha = \frac{\int_{0.19}^{2.2} I_{\text{sol}}(\lambda)(1 - R(\lambda))d\lambda}{\int_{0.19}^{2.5} I_{\text{sol}}(\lambda)d\lambda} \quad (2)$$

$$213 \quad \varepsilon = \frac{\int_{2.5}^{15.4} I_p(\lambda)(1 - R(\lambda))d\lambda}{\int_{2.5}^{15.4} I_p(\lambda)d\lambda} \quad (3)$$

214 The solar spectrum, I_{sol} has an air mass (AM) of 1.5 in accordance with the ISO standard 9845-1
 215 (1992). A key parameter of a selective surface is its selectivity, s , which is defined as a ratio of
 216 the solar absorptance (α) to the emittance (ε)^[36] as given in Eq. (4):

$$217 \quad s = \frac{\alpha}{\varepsilon} \quad (4)$$

218 where α signifies solar absorptance of the coatings estimated in a wavelength range of 190 nm
 219 and 2200 nm while ε is the emittance in a range between 2.5 μm and 15.5 μm .

220

221 3. Results and Discussion

222 3.1. Synchrotron radiation based high resolution XRD studies of the $\text{Cu}_x\text{Co}_y\text{O}_z$ thin film coatings

223 High temperature synchrotron radiation X-ray diffraction (SR-XRD) measurements of
224 $\text{Cu}_x\text{Co}_y\text{O}_z$ with and without graphene oxide were carried out at room temperature, 100, 200 and
225 300 °C in a 2θ geometry from 18° to 44° and 0.002° increment. SR-XRD data presented in Fig. 1
226 provide information with the crystalline structures, phase transitions and thermal stability of
227 these coatings. In CuCoO films, multiple and stable phases e.g., CuO_x , CoO_x , CuCoO_x exist until
228 to 300 °C. However $\text{Cu}_x\text{Co}_y\text{O}_z$ films with 1.5 wt% of graphene oxide, in addition to the above
229 phases, a new phase orthorhombic/ CoCu_2O_3 (space group $P_{mnm}(59)$) was also observed.
230 Monoclinic CuO and hexagonal CoO were the dominant phases in each case (see details in
231 Tables 1 and 2). All the coatings exhibited sharp diffraction lines at all temperatures indicating
232 well defined crystalline phases. Absence of any impurity diffraction peaks reveals that the
233 samples are formed with highly pure precursors. According to Table 1 and Table 2, it is clearly
234 seen that the 2θ positions of all the existing phases are invariant at all measuring temperatures.
235 This reflects the fact that these coatings possess good physical and chemical stability within the
236 operating temperature up to 300 °C. Further observation shows that, with the addition of 1.5 wt%
237 of graphene oxide to the copper-cobalt oxide coatings, 2θ positions of the Bragg reflections are
238 slightly shifting towards the lower angle sides. Due to the lowering of 2θ values the residual
239 stress of the coatings is reduced. The reduction in internal residual stresses result in lattice
240 distortion. As a consequence of all these factors, it is believed that the coatings achieve greater
241 mechanical and thermal stability in the operating temperature range. The existence of CuO and
242 Co_3O_4 phases in Cu–Co spinel was detected by SR-XRD analysis. The phase crystallinity of
243 deposited films is also in good agreement with the reported data for $\text{CoO}^{[37]}$. However, the CuO
244 lines show the relatively low intensity in the X-ray pattern on these coatings. Incorporation of the
245 carbon materials into the mixed metal oxide networks leads to reduction of the scattering

246 intensities of the Bragg reflections. As a result, a subtle shift to smaller d -spacings takes
247 place^[38,39] and spinel structures with enhanced solar selectivity and better physical stability are
248 attained. In these films, copper ions occupy both the tetrahedral and the octahedral sites of the
249 spinels. The difference of ionic radius in the tetrahedral and octahedral sites of copper ions (16
250 pm) and cobalt ions (5.5 pm) also forms a basis for stable structural configurations of these
251 coatings. The films are also stable towards air and moisture having well defined grain
252 boundaries. Cu–Co oxide based thin films form a single phase together with a partially inverted
253 spinel structure^[40–44] and the segregation of Cu and/or Co oxide phases depends on the Cu/Co
254 ratio and annealing temperatures. Compared to other methods the sol–gel dip-coating method
255 allows the preparation of the Co_3O_4 stable phase at relatively low temperature^[45]. Annealing of
256 the coatings promotes the migration of the cobalt towards the surface of the coating, where it is
257 oxidized by the atmospheric oxygen and forms the cobalt oxide layer. In a previous
258 publication^[46], annealing in air at 500 °C showed that the bulk cobalt films migrate towards the
259 coating surface and forms a layer of Co_3O_4 having a thickness of 40–50 nm. Since the mixed
260 CuCo oxide thin films can exist in a variety of compositions and crystal structures, their
261 properties also vary widely. As a result, these coatings show a broad variety of potential
262 applications^[47] such as solar selective surfaces.

263

264 3.2. XPS analysis of the ($\text{Cu}_x\text{Co}_y\text{O}_z$ + graphene oxide) coatings

265 The XPS survey scans (not shown here) of these coatings were conducted before etching
266 and after 2 min etching of each sample. An etching of 2 min was chosen to remove the surface
267 contamination around the coatings. The elemental analyses of the copper cobalt oxide thin film
268 coatings with the addition of various wt% of graphene oxide are presented in Table 3. From

269 Table 3, it is noticed that the carbon content is monotonically increased with the subsequent
270 addition of graphene oxide to the copper cobalt oxide coatings which in turn indicates that the
271 progressive amount of graphene oxide was introduced to the copper cobalt oxide coatings.

272 Fig. 2(a–e) exhibits the deconvolution of the XPS spectra of the $Cu2p_{3/2}$ peak of
273 $Cu_xCo_yO_z$ coatings deposited with various wt.% of GO. The two main peaks of $Cu2p_{3/2}$ and
274 $Cu2p_{1/2}$ ($Cu2p_{1/2}$ are not shown here) have a binding energy difference of 19.9 eV. The difference
275 in binding energy between $Cu2p_{1/2}$ and $Cu2p_{3/2}$ peaks suggests the occurrence of low oxidation
276 states of copper. Our findings herein are in accord with earlier reports^[30,48]. Compared to the
277 CuO, the covalent nature of the Cu–O bond in copper cobaltite was reduced due to the higher
278 intensity of the satellite peak^[49]. The deconvolution of $Cu2p_{3/2}$ photoelectron lines illustrates two
279 curve-fitting components in the vicinity of 932–934.5 eV. The main $Cu2p_{3/2}$ peaks around 932–
280 933 eV are due to the metal (octahedral) Cu^+ ions whereas peaks due to the Cu^{2+} ions were found
281 at 934–935 eV. It is believed that the $Cu2p_{3/2}$ photoelectron peaks reveal the tetrahedral Cu^+ with
282 its counterpart peak from the octahedral $Cu^{+[50]}$. The $Cu2p_{3/2}$ photoelectron peak with shake-up
283 satellite is ascribed to the copper oxides. In copper cobalt oxide system, the reduction of Cu^{2+} to
284 Cu^+ has been previously detected^[49,51]. The oxidation state of copper with different coordinations
285 is possibly due to the evolution of Cu^{2+} A-sites originating from the disintegration during the
286 high-temperature annealing at 500 °C. Other reports mentioned that portion of octahedral Cu^{2+}
287 (satellites of cupric oxide) further reduced to octahedral $Cu^{+[52,53]}$. The Cu^{2+} ions are merged into
288 the surface octahedral vacancy, accommodating oxygen with neighboring Co^{2+} ions and thereby
289 forming Cu–O–Co like species^[49,54]. The Cu^+ and Cu^{2+} ions indicate the presence of Cu_2O and
290 CuO in the copper-cobalt system. The presence of CuO was also confirmed by our synchrotron
291 radiation XRD studies.

292 The XPS spectra of the $Co2p$ peaks and the decomposition of the $Co2p_{3/2}$ peak of copper-
 293 cobalt oxide thin film coatings synthesized with various wt% of graphene oxide are presented in
 294 Fig. 3(a–e). In each of the $Co2p$ spectrum, two main peaks are assigned as $Co2p_{3/2}$ and $Co2p_{3/2}$,
 295 along with a satellite in the neighbourhood of the higher binding energy region of each peaks. In
 296 each coating, the peak-fitting of $Co2p_{3/2}$ and its satellite give rises to three components (See Fig.
 297 3(a–e)). Peaks $Co2p_{3/2}$ and $Co2p_{3/2}$ are separated (not shown here) with binding energy of ~ 16
 298 eV due to the spin-orbit coupling of mixed Co^{2+} and Co^{3+} ions. The existence of the satellite in
 299 the neighbourhood of $Co2p_{3/2}$ peak implies that the feature of Co ions is occupied in a partial
 300 spinel crystal structure. The low intensity of the satellites also confirms the presence of Co^{3+} ions
 301 mixing with Co^{2+} ions^[41]. The components i and ii are due to the formation of Co_3O_4 , and Co_2O_3
 302 which are mostly due to octahedral Co^{3+} or mixed Co^{2+} and Co^{3+} bonding states.

303 Formation of Co_3O_4 was also revealed in the high resolution X-ray diffraction studies
 304 employed by synchrotron radiation. Since the binding energy of Co^{2+} is higher than that of Co^{3+} ,
 305 the shake-up satellite was mostly recorded above 785 eV and is identified to be contributed from
 306 cobalt oxide bonds. From the $Cu2p_{3/2}$ features, characteristic of copper (Cu^{+2}) oxides in
 307 tetrahedral coordination, it is seen that the Cu^{2+} ions partially substitute the Co^{2+} ions thus
 308 forming a lower degree of crystallization of $Cu^{2+}Co^{3+}O_4$ spinel systems^[9,30].

309 Fig. 4(a–e) demonstrates the $O1s$ XPS spectra and the corresponding curve-fitting arisen
 310 from the decomposition $O1s$ peak of $Cu_xCo_yO_z$ coatings without and with various wt.% of
 311 graphene oxide. The decomposition of $O1s$ peak and the satellite give out three curve fitting
 312 components (Fig. 4(a–e)). All the $O1s$ spectrum shows a strong peak with a shoulder at the high
 313 energy side which is a typical feature of $Cu_xCo_yO_z$ coatings^[9]. Comparatively, flat shoulder peak
 314 in the high energy side of $O1s$ peak arises from the high volume fraction of surface oxygen and

315 the low amount of subsurface oxygen in the coated films. Further, the shoulders at the high
316 energy side of the O1s peaks are the characteristic feature of the copper-cobalt oxide systems
317 that differentiates them from O1s on Co₃O₄^[9]. The decoupling curve-fitting peaks (on the lower
318 energy side) are mostly due to the lattice O²⁻ in a Co₃O₄ spinel structure while the other peaks
319 (on the higher energy side) are due to the OH-originated groups *e.g.*, carbonate, hydroxyl
320 etc^[9,41,49,55,56]. It is also assumed that these peaks are arisen from (Cu–O, Co–O) covalent
321 bonds^[30,41].

322 The deconvolution of high resolution C1s XPS data and their corresponding peak-fitting
323 of copper fitting components above 286 eV and 288 eV are the surface contamination of the
324 oxygen, surface oxygen such as chemisorbed water or chemisorbed oxygen O⁻ etc introduced
325 during the synthesis and annealing processes of the thin film coatings. In a bulk structure, the
326 oxygen ions near the surface, generally, have lower electron density than the lattice O²⁻ ions^[57].
327 It is also seen that the coordination number of oxygen ions is much smaller than in cobalt oxide
328 thin film coatings with and without the addition of various wt.% of graphene oxide (Fig. 5). The
329 C1s XPS spectra display a single peak at 284.6 eV together with an asymmetrical tail at high
330 energy side. The principal component of decoupled peak represents the graphitic carbon or
331 hydrocarbon bonds (C–C/C–H bonds) at 284.60 eV and the remainder a regular site together
332 with stronger metal-oxygen assigned as C–OH/C–O–C and C=O/O=C–O structures originated
333 from graphite stacking material^[58]. In Ref. [59], π – π^* shake-up at higher energy side
334 corresponding to sp^2 hybridized carbon was noticed. However, in the present investigation no π –
335 π^* shake-up was identified. A reduction in the peak intensities of C=O/O=C–O bonds was seen
336 on the deconvoluted C1s peak and indicates the incomplete removal of the carbonyl, hydroxyl,
337 and epoxy groups (originated from the oxidation and destruction of the sp^2 bonded pristine

338 graphene) after the heat treatment^[60]. The C=O bonds were detected at 288.01–288.40 eV which
339 eventually confirmed the presence of C=O bonds observed in O1s spectra at 531.33–531.44 eV.
340 Detailed XPS results of $\text{Cu}_x\text{Co}_y\text{O}_z$ and $\text{Cu}_x\text{Co}_y\text{O}_z/\text{graphene oxide}$ coatings are tabulated in Table
341 4. The XPS fitting curves of $\text{Cu}2p_{3/2}$, $\text{Co}2p_{3/2}$, O1s and C1s spectra were analysed via CASA
342 XPS 2.3.1.5 software. A slight change in peaks broadening and peaks shifting towards the lower
343 binding energy was noticed while controlled amount of graphene oxide were incorporated to the
344 sol-gel derived copper-cobalt oxide coatings. This peak shifting and peak broadening indicates
345 the appearance of the reduced states of Cu and Co species on the surface. This also reveals the
346 occurrence of a larger number of oxygen vacancies around the surface of the films. However, a
347 subtle peak shift observed in C1s peak towards the higher binding energies reveals that the
348 presence of graphene oxide modifies the bonding environments of the carbon atoms. It is
349 probably due to the variation in the relative proportions of carbon-carbon and carbon-oxygen
350 contributions. The XPS-peak intensity of all the five samples is identical although measured peak
351 intensities varied significantly with the addition of graphene oxide to the copper-cobalt oxide
352 films. However, to realize the substantial information of measured XPS peak intensities depth
353 profile analysis of the atoms is essential.

354

355 3.3. Energy band-gaps of ($\text{Cu}_x\text{Co}_y\text{O}_z$ + graphene oxide) coatings

356 The UV-Vis absorbance spectra presented in Fig. 6 were used to inspect the optically
357 induced transition and to acquire information about the band structure of the films. Fig. 6 shows
358 that in the visible range of the spectra, the solar absorbance of these coatings increases with the
359 increase in wavelengths. At a wavelength of 350–460 nm, the absorbance values reach its
360 maximum and then decreases. Another maxima was detected at a wavelength of 1360–1500 nm.

361 The spectral dependence of α on the photon energy ($h\nu$) helps to estimate the energy
362 band-gaps of a material. Photon absorptions in crystalline and amorphous materials are known to
363 follow the Tauc relation as given in Eq. (1). The energy band-gap, E_g involved in CuCoO
364 coatings with and without the addition of graphene oxide was estimated by Tauc plot, by plotting
365 the function $(\alpha h\nu)^2$ vs $h\nu$ (the photon energy), by extrapolating the linear portion of the curve to
366 zero absorption. Tauc plots of $h\nu$ vs $(\alpha h\nu)^2$ for CuCoO coatings with and without the addition of
367 graphene oxide films are shown in Fig. 7 and energy gaps were estimated from the intercepts of
368 the linear part of the curves extrapolated to zero in the photon energy axis. The energy band-gap
369 values computed for CuCoO coatings with and without the addition of graphene oxide films are
370 presented in Table 5. The values of direct and indirect transition energy gaps lie between 1.6 and
371 2.4 eV. From Table 5 it is found that the energy band-gaps of CuCoO coatings slightly decrease
372 with the subsequent incorporation of graphene oxide to the CuCoO system. This decrease in
373 energy band-gaps play significant role in enhancing the photon absorption capability of these
374 coatings with the subsequent addition of graphene oxide to the CuCoO matrix.

375 3.4. Optical properties of mixed ($Cu_xCo_yO_z$ + graphene oxide) coatings

376 Fig. 8 shows the UV-Vis spectra of $Cu_xCo_yO_z$ thin film coatings on aluminum substrates
377 with and without the progressive addition of graphene oxide. The solar absorptance of the
378 coatings was calculated based on the AM1.5 solar spectrum standard using the hemispherical
379 reflectance data. This was recorded via UV-Vis-NIR Jasco V-670 double beam
380 spectrophotometer with 60 mm integrating sphere in the wavelength range of 190 to 2200 nm.
381 The solar absorptance values estimated in terms of reflectance as described by Duffie and
382 Beckman^[35] are displayed in Table 6. The UV-Vis reflectance data presented in Fig. 8, indicate
383 that the coatings offer low reflectance (<50%) to UV light, moderate reflectance (<80%) in the

384 visible spectrum and high reflectance (up to 100%) in the region from infrared to far-infrared of
385 the solar spectrum. In the shorter wavelength region, all the UV-Vis spectra are similar showing
386 an interference peaks and absorption edges which is consistent with previous study by Amir *et*
387 *al.* [7]. The solar absorptance of the coatings without graphene oxide was found to be 83.4%,
388 however with the addition of 1.5 wt% of graphene oxide, the absorptance increased to 86.14%.
389 Thus, the introduction of controlled amount of graphene oxide to the $\text{Cu}_x\text{Co}_y\text{O}_z$ thin film
390 coatings, the solar absorptance increased significantly. This superior absorptance would make
391 them smart candidates for their practical application as a selective surface. This result is in good
392 agreement with earlier reported sol-gel derived coatings^[61–63]. Optical absorptance of the
393 copper–cobalt oxide films is influenced by the film thickness, the composition of the substrate,
394 the roughness of the film surface and surface pores among others. Aluminium substrate was used
395 for the films because of its low cost and high reflectivity^[6]. The highly reflective aluminium
396 surface serves to reflect back the infra-red radiation that penetrates the film coating. The copper-
397 cobalt films deposited on the aluminium substrate significantly exhibit higher degree of solar
398 absorption compared to that deposited on a glass substrate^[6]. A rough surface results in a
399 decrease in reflection of the incident solar energy from the surface and the refractive index is
400 reduced by the presence of pores in the $\text{Cu}_x\text{Co}_y\text{O}_z$ graphene oxide surface. These factors promote
401 the solar absorptance by means of multiple reflections and resonant scattering in the pores.

402 Fig. 9 shows the FTIR spectra of $\text{Cu}_x\text{Co}_y\text{O}_z$ thin film coatings with and without the
403 addition of graphene oxide in the wavelength range of 2.5 to 15.5 μm . The thermal emittance of
404 the coatings was calculated in terms of reflectance as described by Duffie and Beckman^[35] and
405 the corresponding solar selectivity was computed. Results of such calculations are displayed in
406 Table 6. From our measurements, it is observed that in the infra-red and far infra-red region, the

407 solar emittance of the coatings decreased significantly with the progressive addition of the
408 graphene oxide to the $\text{Cu}_x\text{Co}_y\text{O}_z$ thin film coatings. This reveals that graphene oxide plays a
409 remarkable role in improving the selectivity of the $\text{Cu}_x\text{Co}_y\text{O}_z$ coatings which reduces the energy
410 loss of the selective surface substantially in the infrared region of the spectrum. In all coatings,
411 interference peak and absorption edge were detected at the shorter wavelength sides. It is well
412 known that the interference peaks and the absorption edges are shifted towards the longer
413 wavelengths regions subsequently when graphene oxide was added to the copper-cobalt films.
414 With the incorporation of 1.5 wt% of graphene oxide in the copper-cobalt oxide films, a highest
415 absorptance of 95.19% was achieved while the average absorptance calculated via D-B
416 method^[35] was 86.14%. Relatively weaker phonon absorption in the vicinity of the wavelength
417 range of 15 μm is also typically exhibited by the copper-cobalt oxide system. Following the same
418 method as described in Ref. [35], an average thermal emittance of 2.97% was recorded by the
419 copper-cobalt coatings doped with 1.5 wt% of graphene oxide and thereby a high solar
420 selectivity of 29.01 was attained for this coating. The increase of absorptance after the addition
421 of graphene oxide is referred to the reduction of reflective properties of coating surface. This
422 variation of reflective properties is attributed to the interference phenomena governed by film
423 thickness and refractive index ratios. A non-uniform and inhomogeneous surface reduces the
424 reflection of the incoming solar radiation at the film surface together with the lower refractive
425 index. At the same time, multiple reflections and resonant scattering of the incident solar
426 radiation also take place around the film surface^[64]. As a result, the solar absorptance is raised up
427 due to the interaction and relaxation mechanisms in the coatings. The higher value of solar
428 absorptance appears to be very promising for application of solar selective surface in
429 photothermal collectors. Compared with other reports for sol-gel derived coatings whereby their

430 $\alpha = 83\%$ ^[63], 80% – 85% ^[61] and 80% ^[62], our findings are quite encouraging. We further assume
431 that the highly reflective aluminium substrates benefits to reflect back the infrared light that pass
432 through the coatings without being absorbed. The transmitted light is reflected back by the
433 substrate which increases the reflectance and reduces the absorptance in the near infrared (NIR)
434 range. As a result, a dark mirror absorber-reflector tandem concept is virtually produced. The
435 solar absorptance and emittance data manifest the fact that addition of a controlled amount of
436 graphene oxide to the copper cobalt oxide coating increases solar selectivity due to the high
437 absorptance in the visible region and increased reflectance in the region from infrared to far-
438 infrared of the solar spectrum. Thus, copper–cobalt oxide thin film coatings with the addition of
439 graphene oxide have a great potential to form the basis of an absorber material for solar selective
440 surface applications in photothermal devices.

441

442 **4. Conclusion**

443 The structural characterization, solar selectivity and X-ray photoelectron spectroscopic
444 investigations of the sol-gel derived copper-cobalt oxide thin film coatings with addition of
445 graphene oxide has been investigated. Synchrotron radiation-based high resolution XRD tests
446 show existence of physically, thermally and chemically stable multiple phases. The energy band-
447 gaps of these coatings were found to decrease systematically with the progressive addition of
448 graphene oxide to the CuCoO films. The solar absorptance was found to increase with the
449 progressive addition of graphene oxide to the $\text{Cu}_x\text{Co}_y\text{O}_z$ system while the optical emittance was
450 reduced and thereby the solar selectivity was significant increased. Hence, copper cobalt oxide
451 thin films with the addition of graphene oxide display a good promise as a smart solar selective
452 surface for photothermal applications. Such features are interesting aspects which may be

453 prevalent in future research concerning designs of superior selective surface. In the present study,
454 we have adopted the sol-gel dip coating method to fabricate mixed metal oxides-based thin film
455 coatings. Sol-gel dip-coating is a popular and versatile technique that can produce mixed metal
456 oxides based thin film coatings with very high solar selectivity up to 44.23. Surface analysis of
457 these coatings via XPS route confirmed the presence of various metal oxide phases (*e.g.*, Cu₂O,
458 CuO, Co₃O₄) which protect them from further oxidization and corrosion. As a solar selective
459 surface, these types of coatings possess some unique advantages *e.g.*, easy operation, convenient
460 and environment friendly, higher efficiency coupled with lower processing costs over other
461 conventional techniques.

462

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595 **Table 1.** 2 θ positions, crystal phases, Miller indices and space groups of sol-gel derived596 Cu_xCo_yO_z coatings as observed from synchrotron radiation XRD studies.

2 θ position at room temperature	2 θ position at 100°C	2 θ position at 200°C	2 θ position at 300°C	Crystal structure	Miller index	Space group	JCPDS reference
20.11 (A)	20.09	20.08	20.08	Monoclinic/CuO	(200)	Cc(9)	89-5899
20.48 (B)	20.44	20.46	20.47		(111)		
36.76 (F)	33.75	33.77	33.76		(022)		
41.59 (J)	41.56	41.56	41.58		(222)		
20.11 (A)	20.11	20.10	20.09	Cubic/CoCo ₂ O ₄	(222)	Fd-3m(227)	78-1980
23.28 (C)	23.28	23.26	23.26		(400)		
33.76 (F)	33.75	33.77	33.76		(440)		
39.15 (G)	39.16	39.14	39.13		(622)		
20.11 (A)	20.10	20.09	20.10	Hexagonal/CoO	(101)	P6 ₃ mc(186)	89-2803
33.16 (E)	33.13	33.15	33.14		(103)		
39.91 (H)	39.90	39.89	39.89		(202)		
40.98 (I)	40.96	40.97	40.97		(104)		
23.84 (D)	23.84	23.85	23.83	Rhombohedral/Co CuO ₂	(221)	R-3m(166)	74-1855
33.76 (F)	33.75	33.75	33.75		(444)		
39.91 (H)	39.90	39.88	39.89		(020)		
41.59 (J)	41.58	41.57	41.59		(131)		
39.15 (G)	39.14	39.13	39.13		(316)		

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 608 **Table 2.** 2 θ Positions, crystal phases, Miller indices and space groups of sol-gel derived
 609 (Cu_xCo_yO_z + 1.5 wt% GO) coatings as observed from synchrotron radiation XRD studies.

2 θ position at room temperature	2 θ position at 100°C	2 θ position at 200°C	2 θ position at 300°C	Crystal structure	Miller index	Space group	JCPDS reference
20.10 (A)	20.09	20.08	20.08	Monoclinic/CuO	(200)	Cc(9)	89-5899
20.48 (B)	20.45	20.46	20.47		(111)		
33.74 (F)	33.73	33.74	33.74		(022)		
41.57 (J)	41.56	41.56	41.57		(222)		
20.11 (A)	20.11	20.10	20.09	Cubic/CoCo ₂ O ₃	(222)	Fd-3m(227)	78-1980
23.28 (C)	23.28	23.26	23.26		(400)		
33.76 (F)	33.75	33.77	33.76		(440)		
39.15 (G)	39.16	39.14	39.13		(622)		
20.11 (A)	20.10	20.09	20.10	Hexagonal/CoO	(101)	P6 ₃ mc(186)	89-2803
33.16 (E)	33.13	33.15	33.14		(103)		
39.91 (H)	39.90	39.89	39.89		(202)		
40.98 (I)	40.96	40.97	40.97		(104)		
23.84 (D)	23.82	23.83	23.83	Rhombohedral/ CoCuO ₂	(221)	R-3m(166)	74-1855
33.74 (F)	33.73	33.73	33.74		(444)		
39.90 (H)	39.90	39.89	39.89		(020)		
41.57 (J)	41.57	41.57	41.56		(131)		
20.48 (B)	20.84	20.47	20.47	Orthorhombic/Co Cu ₂ O ₃	(301)	Pmmn(59)	76-0442
23.84 (D)	23.83	23.84	23.83		(020)		
33.74 (F)	33.74	33.73	33.74		(302)		
39.10 (G)	39.10	39.10	39.09		(620)		

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619 **Table 3.** Atomic compositions of $\text{Cu}_x\text{Co}_y\text{O}_z$ thin film coatings with and without graphene oxide

620 addition before and after etching as estimated via XPS measurements.

Samples	Elements	Atomic percentages (at.%) of elements	
		Before etching	After etching
$\text{Cu}_x\text{Co}_y\text{O}_z$	Cu	12.54	28.66
	Co	11.67	33.51
	O	43.11	33.82
	C	32.67	4.01
$\text{Cu}_x\text{Co}_y\text{O}_z$ +0.1wt%GO	Cu	14.46	30.57
	Co	20.58	35.45
	O	40.92	28.66
	C	24.04	5.32
$\text{Cu}_x\text{Co}_y\text{O}_z$ +0.5wt%GO	Cu	19.13	29.87
	Co	20.27	34.66
	O	36.08	30.09
	C	24.52	5.38
$\text{Cu}_x\text{Co}_y\text{O}_z$ +1.0wt%GO	Cu	12.96	30.35
	Co	15.75	36.71
	O	40.55	27.41
	C	30.74	5.54
$\text{Cu}_x\text{Co}_y\text{O}_z$ +1.5wt%GO	Cu	14.41	28.47
	Co	17.83	30.02
	O	39.03	35.19
	C	28.73	6.32

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631 **Table 4.** Fitting results of the XPS data of sol-gel derived $\text{Cu}_x\text{Co}_y\text{O}_z$ coatings with and without

632 graphene oxide addition for the core level binding energies.

Samples	Photoelectron lines	Bonding states	BE (eV)	FWHM (eV)	Percentage of the component (%)
$\text{Cu}_x\text{Co}_y\text{O}_z$	Cu2p3/2	Metal Cu^+ ions (Cu_2O bonds)	932.52(i)	1.70	68.86
		Metal Cu^{2+} ions (CuO bonds)	934.55(ii)	2.00	31.14
	Co2p3/2	Co_3O_4	779.40(i)	2.00	24.54
		Co_2O_3	781.15(ii)	3.26	37.34
	Co2p3/2 sat.	$\text{Co}_3\text{O}_4/\text{Co}_2\text{O}_3$	785.96(iii)	5.96	38.12
	O1s	Metal oxides (Cu/Co oxides)	529.26(i)	1.00	54.33
		Metal oxides (Cu/Co oxides)	529.81(ii)	1.30	28.07
		Surface oxygen/C=O/O=C-O bonds	531.37(iii)	1.30	17.60
	C1s	C-C/C-H bonds	284.40(i)	1.30	60.25
		C-OH/C-O-C bonds	286.28(ii)	1.25	23.01
C=O/O=C-O bonds		288.14(iii)	1.30	16.74	
$\text{Cu}_x\text{Co}_y\text{O}_z + 0.1\text{wt}\%\text{GO}$	Cu2p3/2	Metal Cu^+ ions (Cu_2O bonds)	932.53(i)	1.80	74.03
		Metal Cu^{2+} ions (CuO bonds)	934.45(ii)	2.20	25.97
	Co2p3/2	Co_3O_4	779.15(i)	2.00	30.75
		Co_2O_3	780.94(ii)	3.30	35.29
	Co2p3/2 sat.	$\text{Co}_3\text{O}_4/\text{Co}_2\text{O}_3$	785.78(iii)	6.00	33.96
	O1s	Metal oxides (Cu/Co oxides)	529.24(i)	1.07	60.10
		Metal oxides (Cu/Co oxides)	529.78(ii)	1.35	18.58
		Surface oxygen/C=O/O=C-O bonds	531.13(iii)	1.50	21.31
	C1s	C-C/C-H bonds	284.45(i)	1.32	72.82
		C-OH/C-O-C bonds	286.62(ii)	1.32	14.59
C=O/O=C-O bonds		288.01(iii)	1.32	12.59	
$\text{Cu}_x\text{Co}_y\text{O}_z + 0.5\text{wt}\%\text{GO}$	Cu2p3/2	Metal Cu^+ ions (Cu_2O bonds)	932.40(i)	1.70	73.97
		Metal Cu^{2+} ions (CuO bonds)	934.30(ii)	1.74	26.03
	Co2p3/2	Co_3O_4	779.12(i)	2.00	28.66
		Co_2O_3	780.86(ii)	3.30	34.08
	Co2p3/2 sat.	$\text{Co}_3\text{O}_4/\text{Co}_2\text{O}_3$	785.71(iii)	5.97	37.25
	O1s	Metal oxides (Cu/Co oxides)	529.15(i)	1.08	63.38
		Metal oxides (Cu/Co oxides)	529.71(ii)	1.32	13.97
		Surface oxygen/C=O/O=C-O bonds	531.10(iii)	1.68	22.65
	C1s	C-C/C-H bonds	284.34(i)	1.34	78.09
		C-OH/C-O-C bonds	286.79(ii)	1.32	11.24
C=O/O=C-O bonds		288.58(iii)	1.33	10.68	
$\text{Cu}_x\text{Co}_y\text{O}_z + 1\text{wt}\%\text{GO}$	Cu2p3/2	Metal Cu^+ ions (Cu_2O bonds)	932.34(i)	1.77	67.96
		Metal Cu^{2+} ions (CuO bonds)	934.28(ii)	2.20	32.04
	Co2p3/2	Co_3O_4	779.08(i)	2.00	25.47
		Co_2O_3	780.80(ii)	3.29	37.26
	Co2p3/2 sat.	$\text{Co}_3\text{O}_4/\text{Co}_2\text{O}_3$	785.67(iii)	5.99	37.27
	O1s	Metal oxides (Cu/Co oxides)	529.06(i)	1.10	61.14
Metal oxides (Cu/Co oxides)		529.49(ii)	1.35	28.93	
		Surface oxygen/C=O/O=C-O bonds	530.98(iii)	1.39	9.93

		C-C/C-H bonds	284.37(i)	1.40	62.84
	C1s	C-OH/C-O-C bonds	286.32(ii)	1.36	10.05
		C=O/O=C-O bonds	288.15(iii)	1.35	27.00
Cu _x Co _y O _z + 1.5wt%GO	Cu2p3/2	Metal Cu ⁺ ions (Cu ₂ O bonds)	932.30(i)	1.70	68.08
		Metal Cu ²⁺ ions (CuO bonds)	934.25(ii)	2.20	31.92
	Co2p3/2	Co ₃ O ₄	779.07(i)	2.08	30.65
		Co ₂ O ₃	780.73(ii)	3.30	33.33
	Co2p3/2 sat.	Co ₃ O ₄ /Co ₂ O ₃	785.64(iii)	5.99	36.02
	O1s	Metal oxides (Cu/Co oxides)	529.03(i)	1.08	80.16
		Metal oxides (Cu/Co oxides)	529.45(ii)	1.37	9.65
		Surface oxygen/C=O/O=C-O bonds	530.98(iii)	1.35	10.19
	C1s	C-C/C-H bonds	284.60(i)	1.37	77.68
		C-OH/C-O-C bonds	286.55(ii)	1.35	15.17
C=O/O=C-O bonds		288.81(iii)	1.34	7.14	

633 Note: (i) – (iii) notations in the BE column indicate the component parts of deconvoluted high
 634 resolution XPS spectra of Figs. 2-5.

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Table 5. Energy band-gaps of Cu_xCo_yO_z thin film coatings with the addition of graphene oxide.

Coatings name	Band-gap, E_g (eV)
Cu _x Co _y O _z	2.4
Cu _x Co _y O _z + 0.1wt% GO	2.2
Cu _x Co _y O _z + 0.5wt% GO	2.1
Cu _x Co _y O _z + 1wt% GO	1.7
Cu _x Co _y O _z + 1.5wt% GO	1.6

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Table 6. Optical properties of the Cu_xCo_yO_z thin film coatings with the addition of graphene oxide.

Sample compositions	Absorptance, α (%)	Emittance, ε (%)	Selectivity, $s = \alpha/\varepsilon$
Cu _x Co _y O _z	83.40	5.70	14.63
Cu _x Co _y O _z + 0.1wt% GO	84.00	5.27	15.85
Cu _x Co _y O _z + 0.5wt% GO	84.30	4.80	17.56
Cu _x Co _y O _z + 1wt% GO	85.60	3.20	26.75
Cu _x Co _y O _z + 1.5wt% GO	86.14	2.97	29.01

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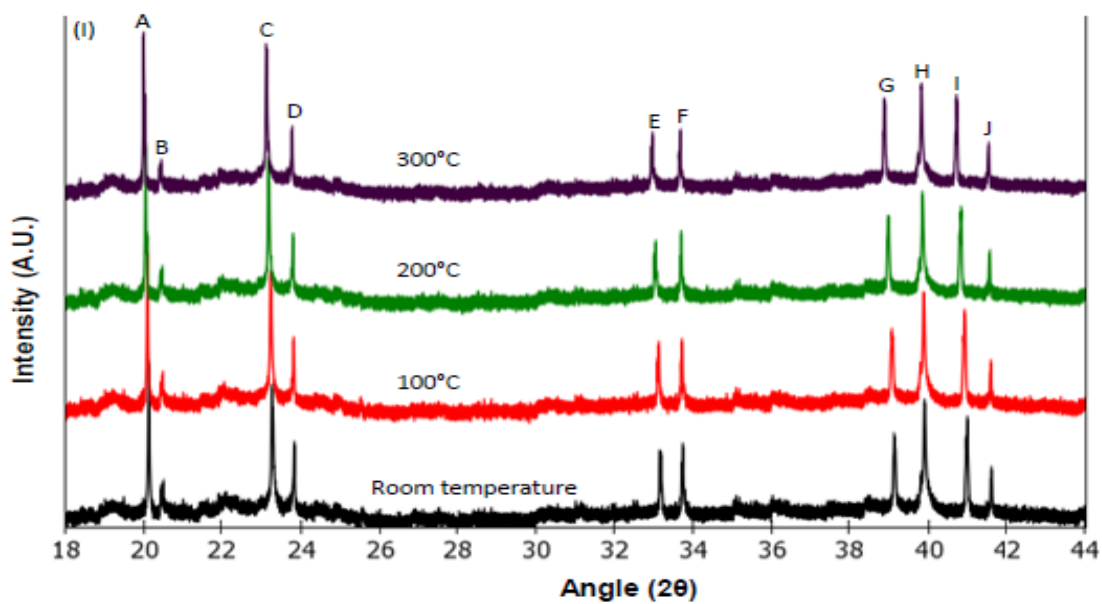
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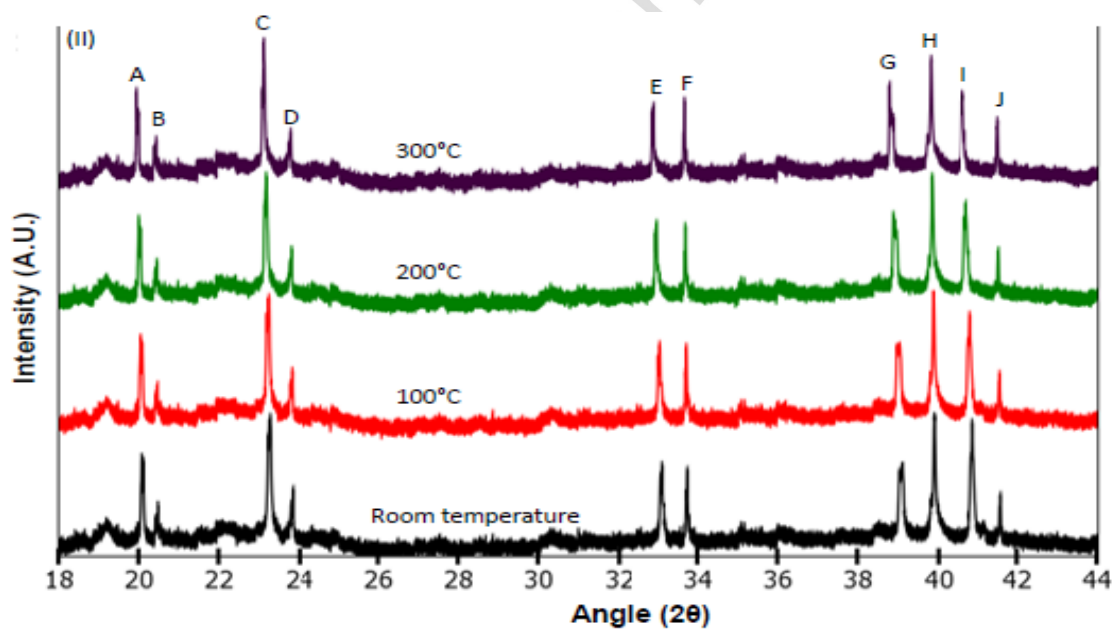
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Fig. 1. Synchrotron radiation X-ray diffraction data of (A) $\text{Cu}_x\text{Co}_y\text{O}_z$ coatings, and (B)

$\text{Cu}_x\text{Co}_y\text{O}_z$ thin film coatings with 1.5 wt% of graphene oxide at room temperature, 100 °C,

200 °C, and 300 °C acquired at the powder diffraction beamline at Australian Synchrotron,

Melbourne.

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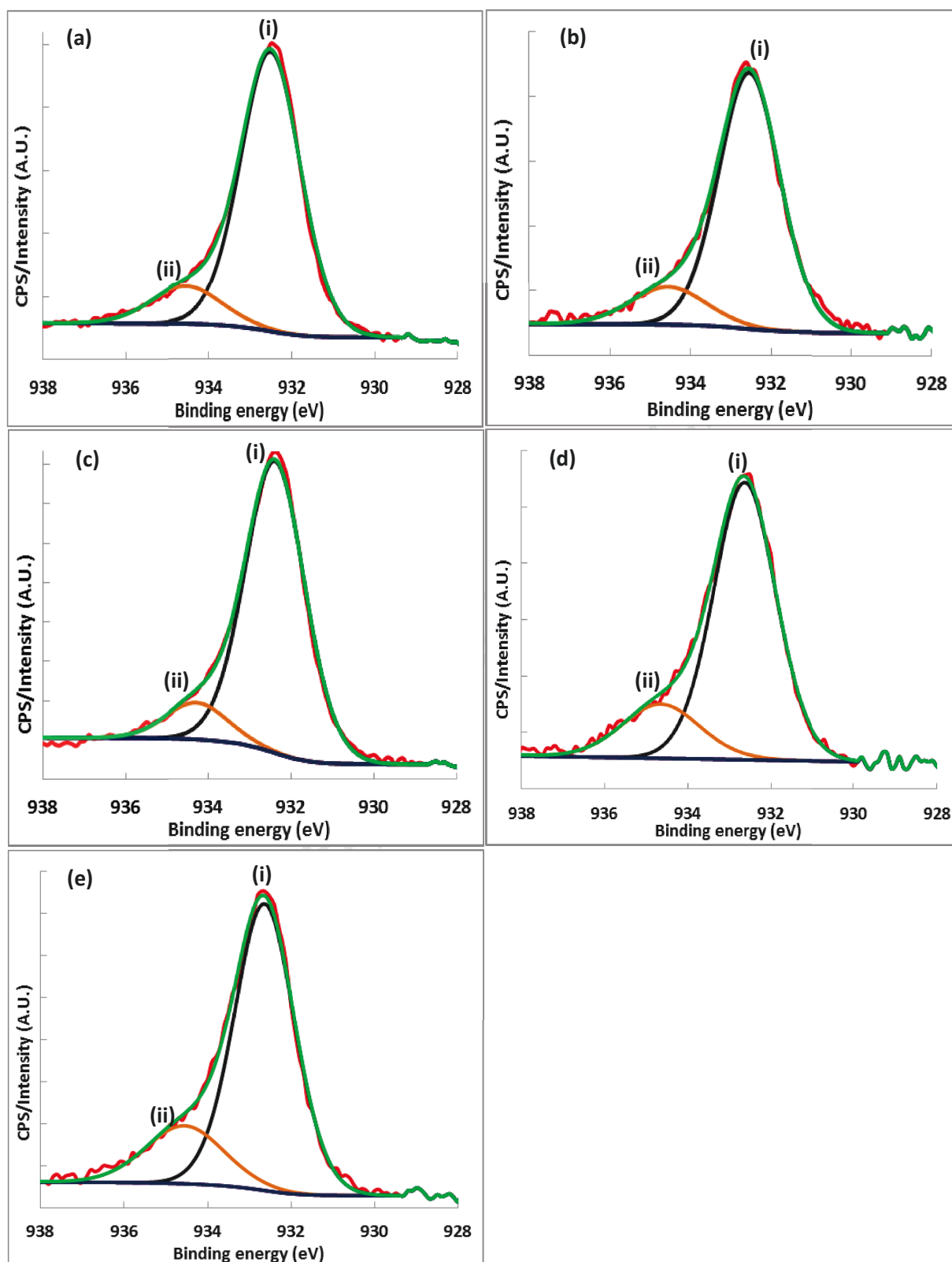


Fig. 2. Decoupling of XPS spectra of $\text{Cu}2p_{3/2}$ peak of CuCoO thin film coatings: (a) $\text{Cu}_x\text{Co}_y\text{O}_z$ (b) $\text{Cu}_x\text{Co}_y\text{O}_z + 0.1\text{wt.}\% \text{GO}$, (c) $\text{Cu}_x\text{Co}_y\text{O}_z + 0.5\text{wt.}\% \text{GO}$, (d) $\text{Cu}_x\text{Co}_y\text{O}_z + 1\text{wt.}\% \text{GO}$, (e) $\text{Cu}_x\text{Co}_y\text{O}_z + 1.5\text{wt.}\% \text{GO}$.

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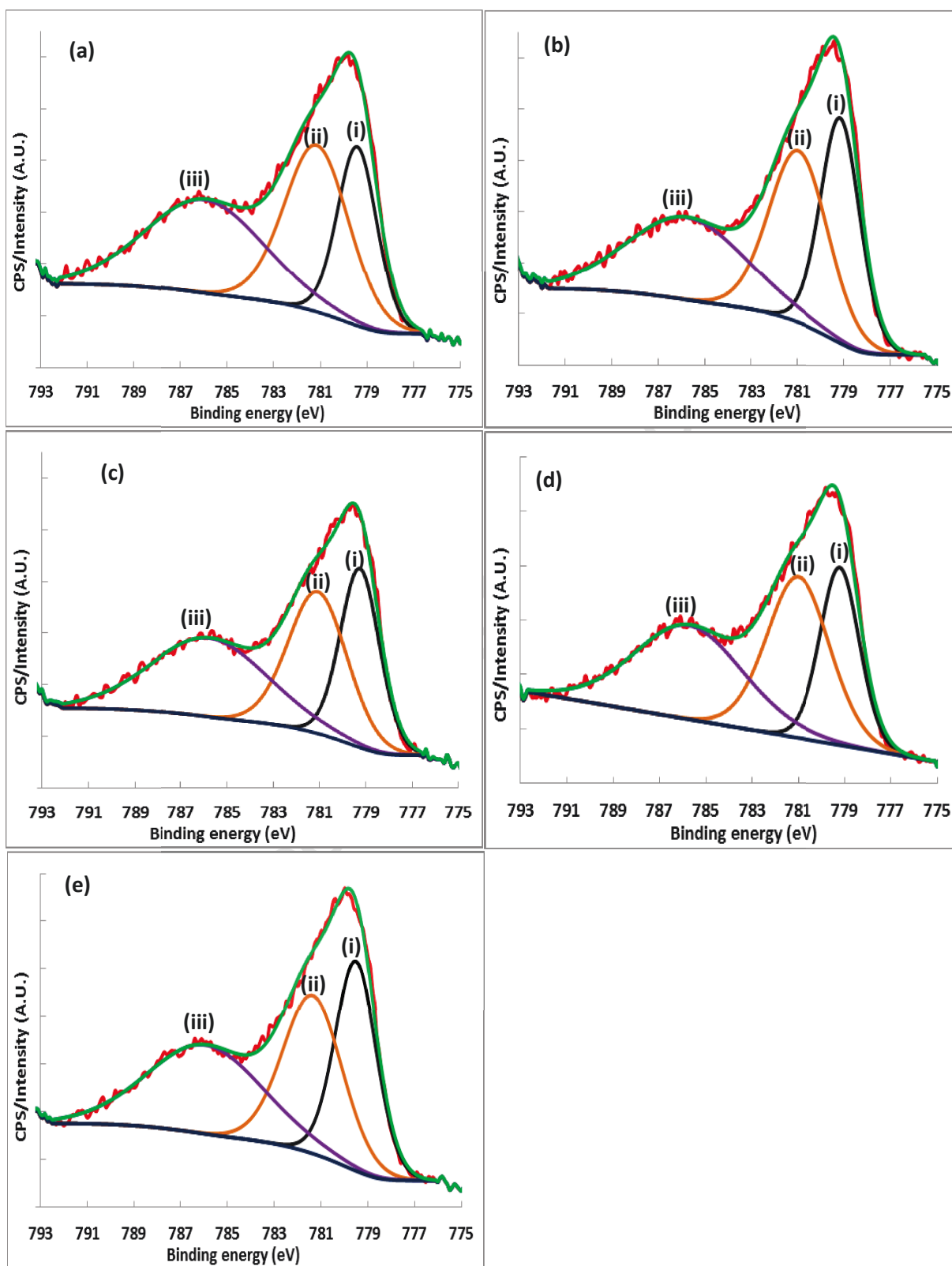


Fig. 3. Decoupling of XPS spectra of Co $2p_{3/2}$ peak of CuCoO thin film coatings: (a) Cu $_x$ Co $_y$ O $_z$ (b) Cu $_x$ Co $_y$ O $_z$ + 0.1wt% GO (c) Cu $_x$ Co $_y$ O $_z$ + 0.5wt% GO (d) Cu $_x$ Co $_y$ O $_z$ + 1wt% GO (e) Cu $_x$ Co $_y$ O $_z$ + 1.5wt% GO.

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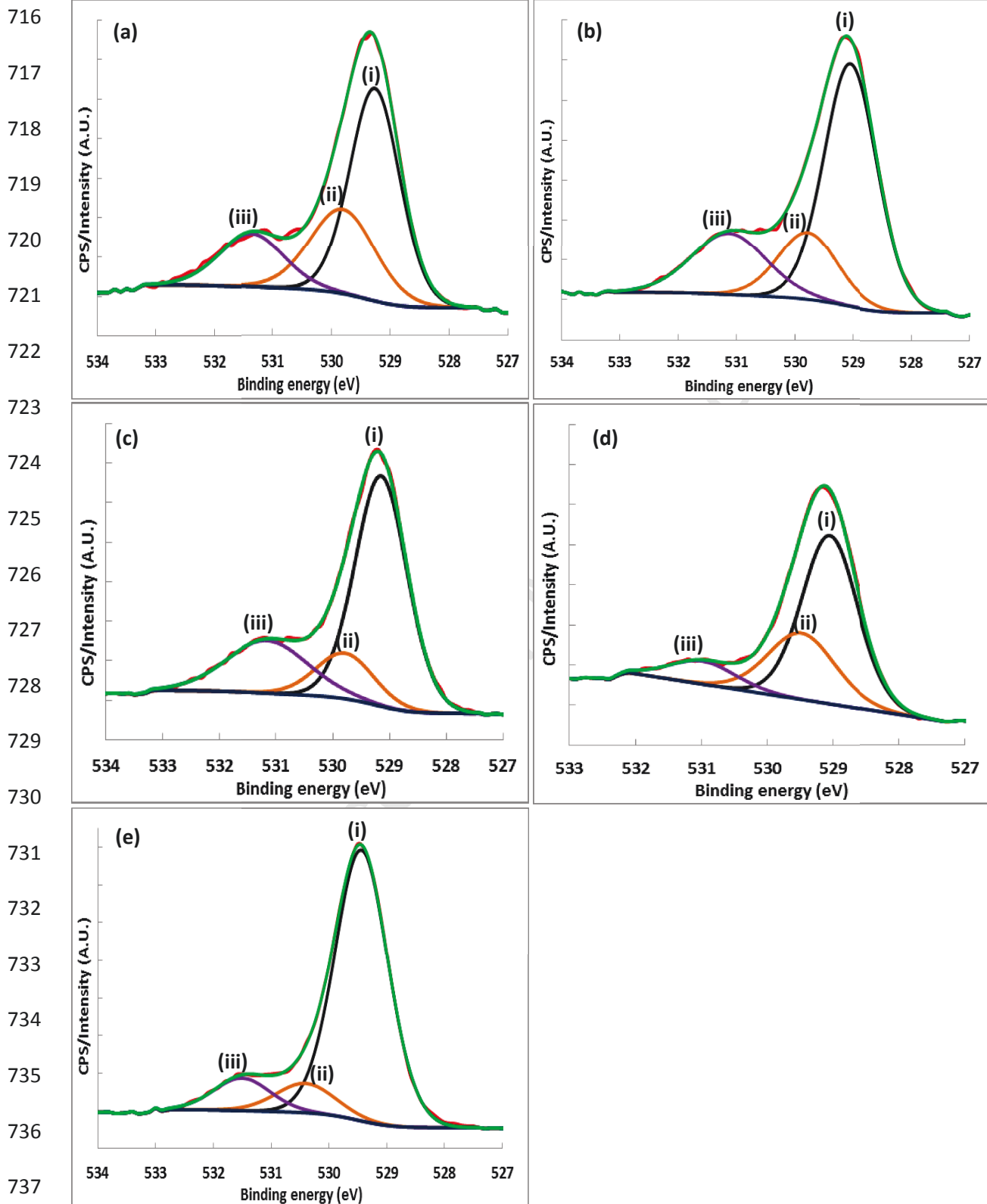


Fig. 4. Decoupling of XPS spectra of O1s peak of CuCoO thin film coatings: (a) $\text{Cu}_x\text{Co}_y\text{O}_z$ (b) $\text{Cu}_x\text{Co}_y\text{O}_z + 0.1\text{wt}\% \text{GO}$ (c) $\text{Cu}_x\text{Co}_y\text{O}_z + 0.5\text{wt}\% \text{GO}$ (d) $\text{Cu}_x\text{Co}_y\text{O}_z + 1\text{wt}\% \text{GO}$ (e) $\text{Cu}_x\text{Co}_y\text{O}_z + 1.5\text{wt}\% \text{GO}$.

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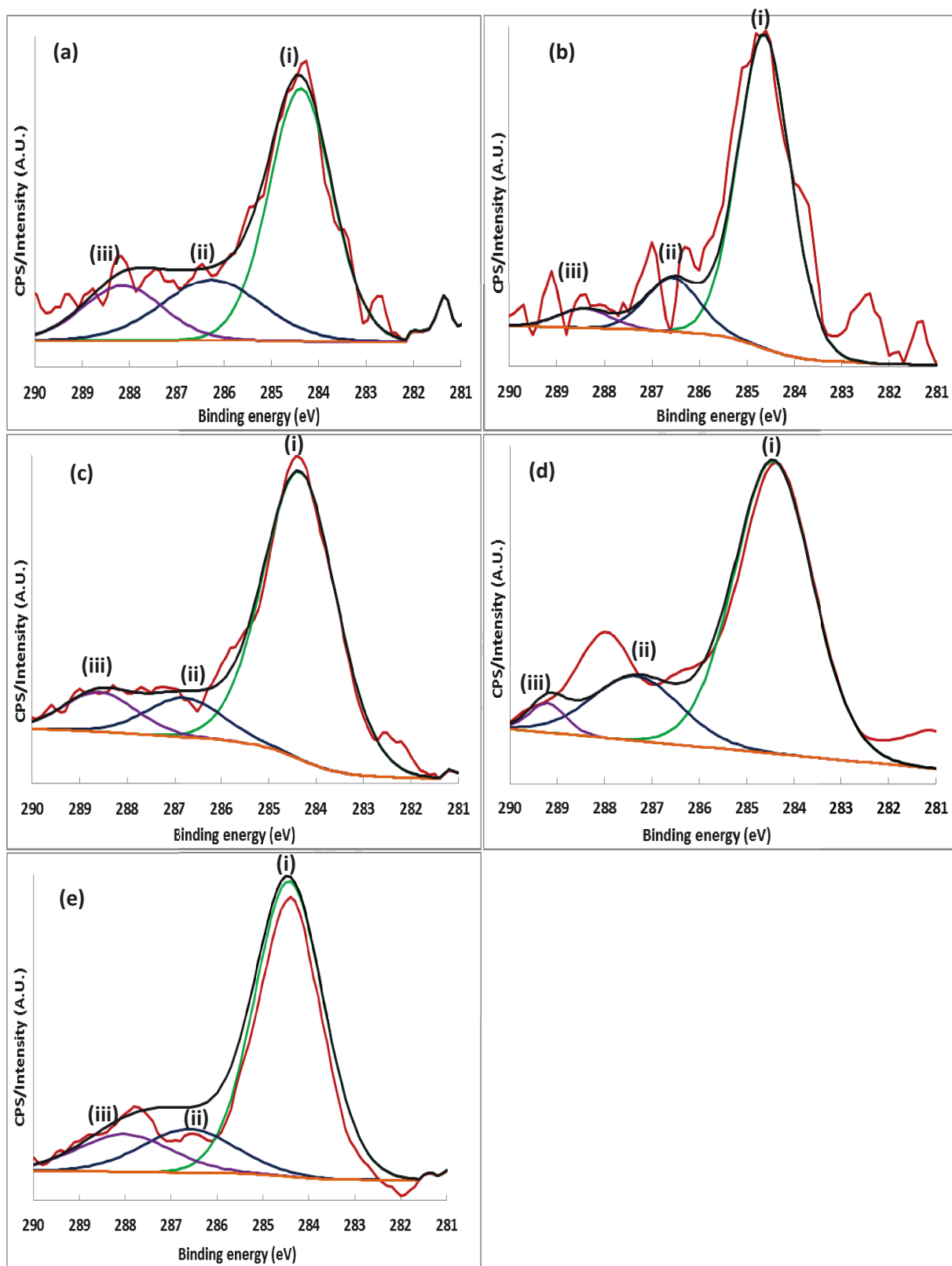


Fig. 5. Decoupling of XPS spectra of C1s peak of CuCoO thin film coatings: (a) $\text{Cu}_x\text{Co}_y\text{O}_z$ (b) $\text{Cu}_x\text{Co}_y\text{O}_z$ + 0.1wt% GO (c) $\text{Cu}_x\text{Co}_y\text{O}_z$ + 0.5wt% GO (d) $\text{Cu}_x\text{Co}_y\text{O}_z$ + 1wt% GO (e) $\text{Cu}_x\text{Co}_y\text{O}_z$ + 1.5wt% GO.

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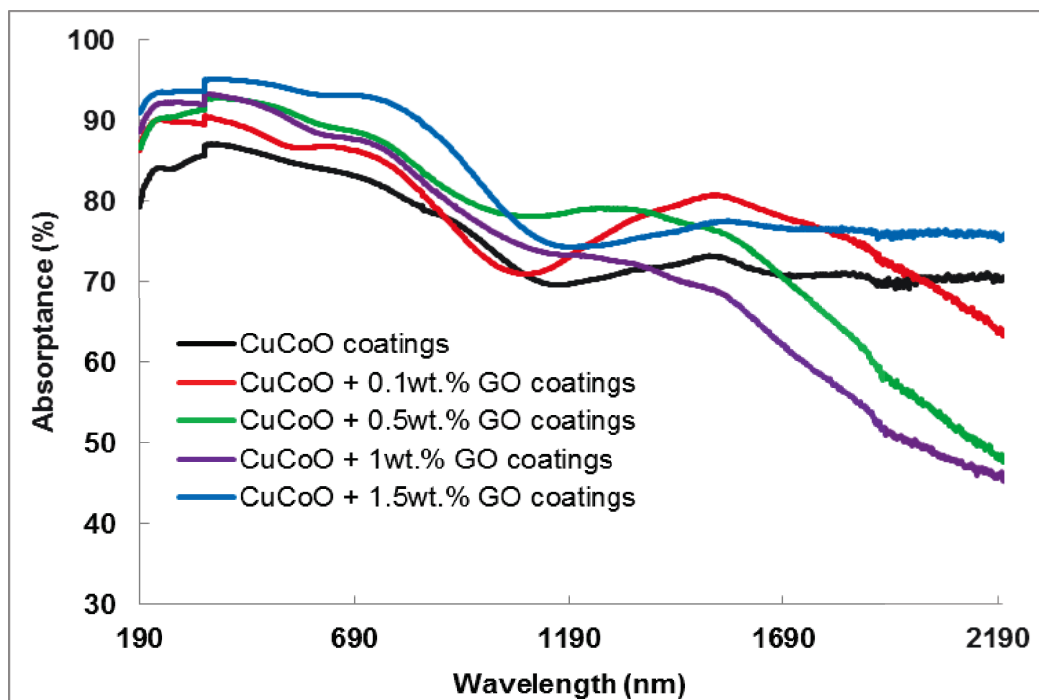
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Fig. 6. UV-Vis absorbance spectra of sol-gel $\text{Cu}_x\text{Co}_y\text{O}_z$ thin film coatings without and with the addition of graphene oxide.

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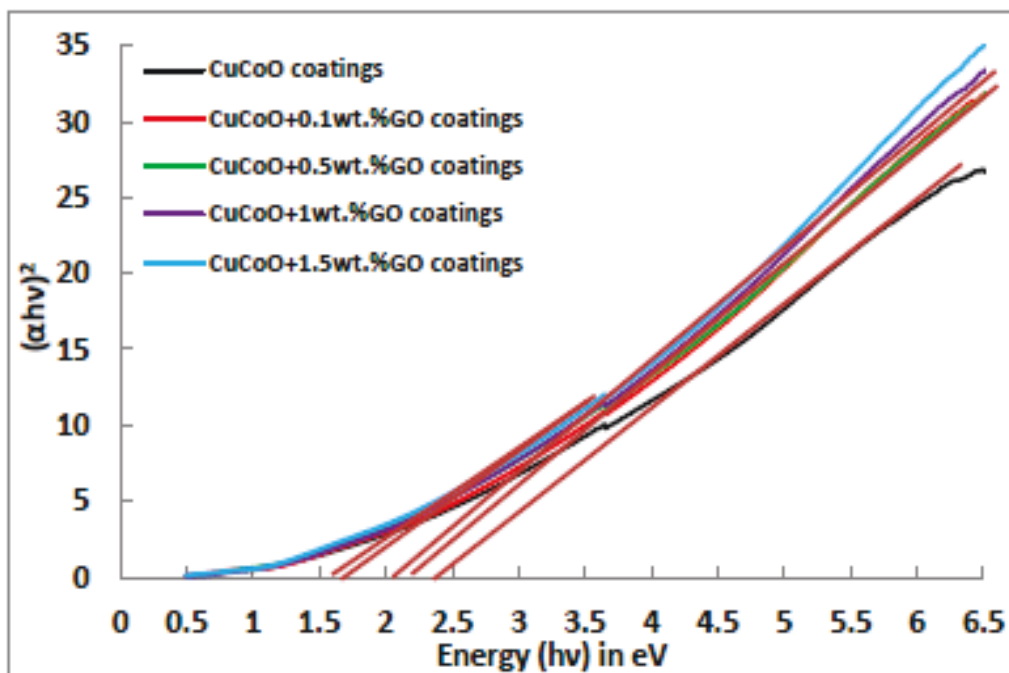


Fig. 7. Estimation of energy band-gaps of sol-gel derived $\text{Cu}_x\text{Co}_y\text{O}_z$ thin film coatings without and with the addition of graphene oxide.

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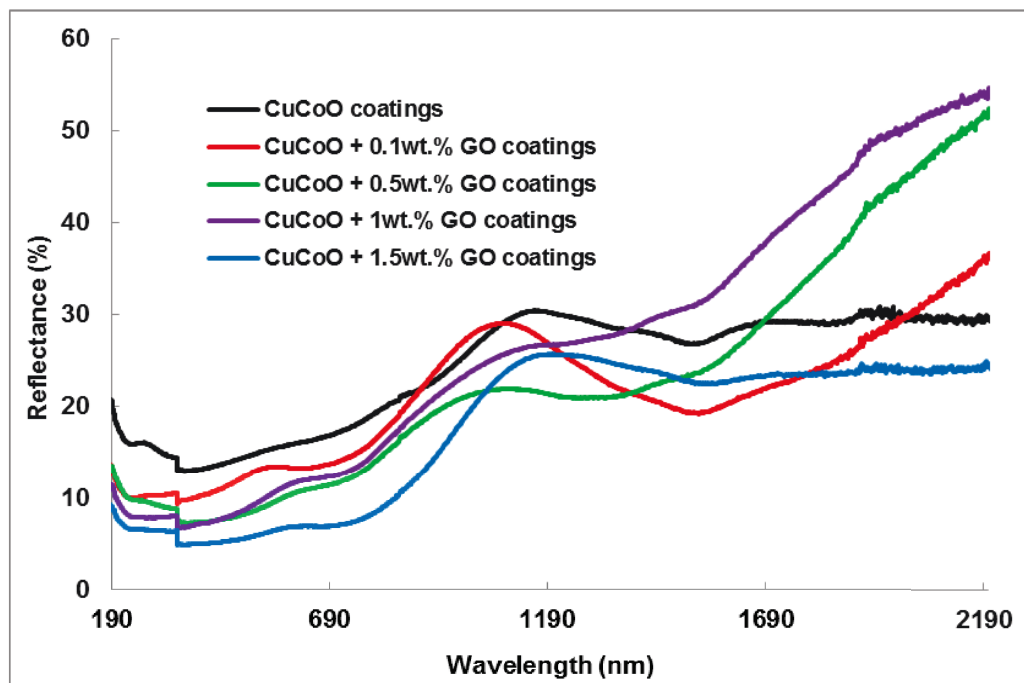


Fig. 8. UV-visible reflectance spectra of $\text{Cu}_x\text{Co}_y\text{O}_z$ thin film coatings without and with the addition of graphene oxide.

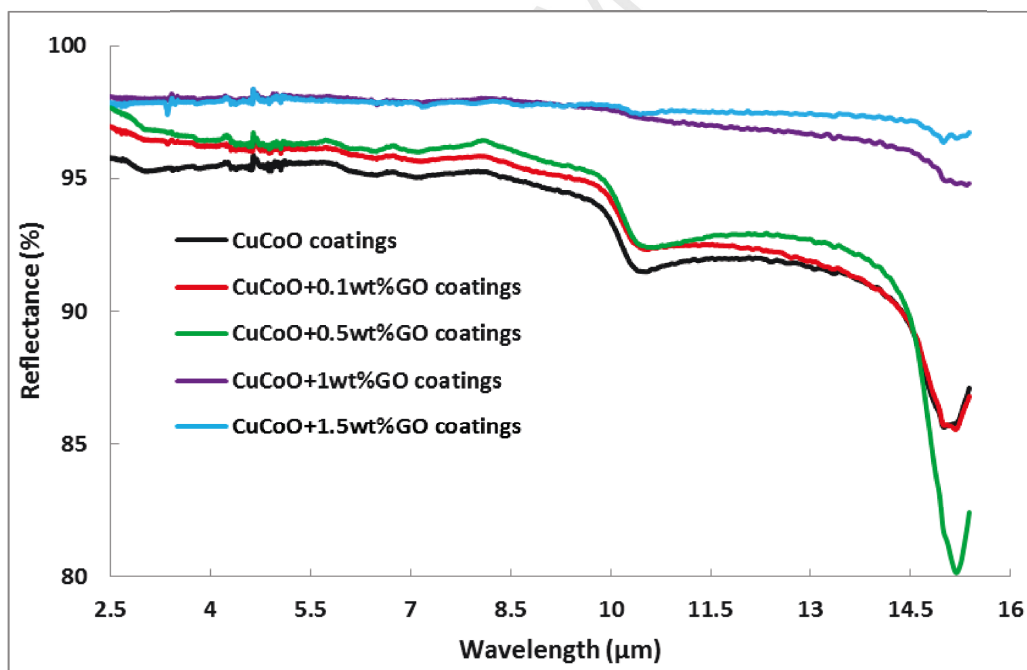


Fig. 9. FTIR reflectance spectra of sol-gel derived $\text{Cu}_x\text{Co}_y\text{O}_z$ coatings without and with the addition of graphene oxide.