Copper-Zinc Oxide Synergistic Approach as Low-Emissivity Material for Energy-Saving Windows

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Abstract. In luxurious glass buildings and constructions, heat gain (or heat loss) mostly comes through the windows. Infrared (IR) radiation is an important factor that causes the entry of heat into the buildings. To save energy consumption of air conditioners, low-emissivity (Low-E) glass coating applications are focused. In the energy-saving field, transparent conductive oxide (TCOs) are used as coatings to minimized IR entry. In this work, copper-doped zinc oxide (CZO) is synthesized for thermal reflective material. Cu(II) ions are doped to ZnO by a sol-gel method to obtain CZO nanoparticles and is coated on a glass substrate. The morphology of CZO is investigated with scanning electron microscopy (SEM); phase crystallinity is determined by X-ray diffraction (XRD); and UV-Vis-NIR spectroscopy is used to characterize UV/IR-shielding and also the optical transparency. IR cameras and in-lab thermal insulation setup are used to test the heat insulation properties. The result shows that 15% copper-doped zinc oxide has the best insulation from IR rays with the lowest temperature in the interior (T3) of 50.6°C while the outer temperature (T2) was at 85.5°C the lowering of the temperature by 34.9°C (cooler by 59%). CZO synthesized from the sol-gel method has promising properties for Low-E glass coating applications.

1. Introduction
It is undeniable that glass buildings look attractive and luxurious. However, glass in building constructions is a poor thermal insulator and it serves as an opening entry to solar radiation. Solar energy distribution comprises of 5% from UV (295 - 400 nm), 50% from visible (400 - 700 nm) and 45% from IR region (700 - 2500 nm). The majority of the IR rays from 700 – 1100 nm radiates heat into the
atmosphere [1]. Blocking of the NIR radiation is an important factor to study in fabricating energy-saving window.

Transparent conductive oxides (TCO) are promising candidates as energy-saving windows because they can reflect (or sometimes absorb) NIR while allowing visible light to be transmitted. Examples of TCO in various applications are indium tin oxide (ITO) used in liquid crystal displays (LCDs) [2], fluorine-doped tin oxide (FTO) in solar cells [3], zirconium-doped indium oxide (ZrIO) in organic light-emitting diodes (OLEDs) [4], indium-doped cadmium oxide (ICO) in optoelectronic devices [5] and more. Zinc oxide (ZnO) by itself absorbs UV and NIR, but is not transparent to visible light. Doping impurity to ZnO, such as, B-doped ZnO, Ti-doped ZnO [6], Al-doped ZnO [7], Sn-doped ZnO [8] are among the many dopings of ZnO that can improve transmission of visible light. Copper-doped ZnO (CZO) is to be considered in this research.

CZO is regarded as a p-type semiconductor. Previous literatures have determined that 5% doping of Cu is the maximum limit to dope into ZnO [9-12]. If the concentration of Cu exceeds 5%, CuO is formed and would result in a p-n junction in the nanoscale, of ZnO as n-type and CuO as p-type [13]. The synergistic effect of ZnO-CuO has been utilized in photocatalytic applications [14].

To obtain CZO nanoparticles, there are many methods from previous research, such as, by sol-gel [15], co-precipitation [16], vapor transport method [17], solvothermal synthesis [18], and RF magnetron sputtering [19]. CZO nanoparticles were used in many applications, for example, photoluminescence, transparent electrode, and electroluminescence material.

The purpose of this work is to fabricate CZO by sol-gel method as a thermal reflective material for energy-saving window coating applications. Different mole percentages of Cu will be loaded to ZnO. Effect of percentage of dopant will be described in this work. Different amount of dopant was varied from 0 to 25 mol% Cu. Calcination conditions were fixed at 550°C for 3 hours. Morphology of CZO particles was determined by SEM; and crystallinity was verified by XRD characterization. IR camera was used to study IR reflective property by detecting the temperature on the surface of the coated glass. An in-lab thermal insulation set-up was used to examine the heat insulation property of CZO nanoparticles.

2. Experimental

2.1. Materials
Zinc acetate dihydrate (Zn(CH$_3$COO)$_2$·2H$_2$O), monoethanolamine (MEA, H$_2$N(CH$_2$CH$_2$OH), antimony doped tin oxide (ATO) and copper (II) acetate monohydrate (Cu(CH$_3$COO)$_2$·H$_2$O) were purchased from Sigma-Aldrich. 2-propanol (CH$_3$C$_2$H$_5$OH) was purchased from Fluka. All chemicals were used without further purification.

2.2. Sol-Gel Preparation of Cu-ZnO
CZO nanoparticles were synthesized following previous research by Jongnavakit et. al. [20] and Saidani et.al. [21]. First, 1 mL of MEA was added to 50 mL isopropanol and stirred for 5 minutes at 65°C. Then Zn(CH$_3$COO)$_2$·2H$_2$O was added to the isopropanol prepared and stirred at 65°C for another 1 hour to make 0.3M zinc-acetate solution (ZnAcetate-solution). Similarly, 0.15M copper-acetate solution (CuAcetate-solution) was prepared from Cu(CH$_3$COO)$_2$·H$_2$O. The CuAcetate-solution was then added drop-wise to ZnAcetate-solution at 0, 1, 5, 10, 15, 20, and 25 mol% Cu. The two solutions were stirred together for another 1 hour at 65°C. The mixtures of ZnAcetate and CuAcetate solutions were of no precipitates. Then the solutions were calcined at 550°C for 3 hours. The final product of CZO nanoparticles were obtained with grey colour.

2.3. Cu-ZnO Characterization
The crystallinity of the nanoparticles was studied with X-ray diffractometer (XRD, D8 Advance Bruker) using Cu Kα radiation operated at step size 0.0200 degrees from 20° to 80° with 1.00 second time per step. The scanning electron micrographs of undoped and Cu-doped ZnO were taken by SU3500 Hitachi at different magnifications from 10 Kx to 100 Kx. All samples of 0 - 25% CZO were prepared with the
same condition. The UV/IR-shielding and optical transparency of the nanoparticle were characterized by UV-Vis-NIR spectrometer (model Carry 5000, Agilent Technologies).

2.4. Thermal insulation properties and application of Cu-ZnO
To study the emissivity of CZO nanoparticles, 100 mg of CZO powder of different mol% Cu were redispersed in isopropanol and coated on a glass slide. Infrared lamp (150 watts) was turned-on and shined onto the glass slide for 120 seconds. Infrared (IR) thermal photographs of the coated glass slide were taken every 30 seconds while the IR-lamp was turned-on and continued to take the thermal images after the lamp was turned-off for another 240 seconds. The infrared thermal camera (Fluke TIS20) was used to determine the temperature on the coated glass surface. The set-up is shown in figure 1. Commercial ATO and bare glass are used as the reference standard for comparison.

To study the thermal insulation property application, an in-lab set-up to mimic a house with a window that is exposed to sunlight was used, set-up shown in figure 2. The coated glass slide was placed on the foam box with a cut out opening with the size of the glass slide. IR lamp (150 watts) shined onto the sample for 60 minutes. The data-logger measured the temperature at T1 (5.5 cm from the light source) with an average temperature of 68.6°C. The data-logger at T2 presents the temperature close to the outer glass surface of each sample. T3 and T4 measure the temperature inside the box where T3 is close to the glass surface and T4 is further away representing the common areas where we would normally stay in a room. All 4 areas (T1 – T4) were measured at every 1 minute and detected by a data-logger (Testo175T3). The set-up is modified from previous work [22].

![Figure 1. Equipment set-up used to determine the emissivity property of CZO nanoparticles.](image1)

![Figure 2. In-lab thermal insulation equipment used to study the thermal insulation property.](image2)

3. Results and Discussion
XRD patterns, figure 3(a), gave many diffraction peaks which implied that ZnO grew in random orientation. Three main peaks of ZnO figure 3(b) corresponded to (100), (002), and (101) indicate that undoped ZnO and Cu-doped ZnO had hexagonal wurtzite structure [23]. With 1 – 5 mol% Cu, the spectrum in figure 3(b) shifted to a higher angle and new absorption peaks were not found because Cu ions were completely substituted in the ZnO lattice [20]. On the other hand, with 10% Cu new absorption peaks appeared at (111) and (200) referring to CuO phase [24, 25]. With 10 – 25 mol% Cu, the more Cu was added, an increase of CuO phase was found due to the excess of Cu ions. This is because the maximum solubility limit of Cu ions in ZnO is 5 mol% [9-12]. When Cu is added in large quantities, some Cu ions will substitute the Zn lattice and some excess Cu filled the vacancy of ZnO lattice resulting in larger particle size and higher intensity of CuO phase [26]. The peak intensity of ZnO decreased with increase mol% of Cu [27]. The intensity of CuO phase in XRD pattern of 15%, 20%, and 25% CZO is
much higher than of 10% CZO because more Cu ions cannot substitute into the ZnO lattice, and CuO phase were formed instead.

Figure 3. XRD spectra of CZO nanoparticle with different mol% of Cu (a) scanning from 20° - 80° and (b) a zoom-in of (a) from 30° – 40° to show the three dominant peaks of ZnO.

From the SEM micrographs in figure 4 when %Cu is less than 10% CZO, samples had the same morphology, this indicate that %Cu had no effect on the morphology of CZO nanoparticles. But when %Cu was greater than 10%, CZO particles showed more spherical shape aggregation as a result of an excess of Cu ions which filled in the vacancy of ZnO lattice. The excess of Cu caused a lattice alteration in 15 - 25% CZO which showed larger particle size than 0 - 10% CZO [16, 27].

Figure 5 plotted the %reflection of CZO in UV-Vis-NIR region from 200 – 2400 nm. In general, there are two types of IR-shielding material. One is NIR reflective material or low-emissivity coating. Another is NIR absorptive material used in solar-thermal energy conversion. UV-Vis-NIR spectra indicate that CZO has ability to reflect wavelengths in the NIR region while commercial ATO has outstanding IR absorption property. Comparing among 1 – 10% CZO in the range of 700 - 1100 nm found that 1% CZO has ability to reflect in NIR region higher than 5% and 10% CZO. For longer wavelength than 1100 nm, 5% and 10%Cu have very similar reflection values, and both 5% and 10% CZO have a better reflection ability than 1% CZO. However, excess mol% of Cu result in less reflection in visible region. In 15 – 25% CZO, they have higher %reflection in both visible and NIR region compare to 1 - 10% CZO this is because of the larger particle size found in 15 – 25% CZO. From these results, 15% CZO is the most reasonable to use for NIR reflective material because the reflection of NIR region is the highest and reflects visible light only about 36%.

Figure 6 plotted the temperatures on the coated glass slide taken from the thermal IR camera while the IR lamp was turned-on (from 0 – 120 seconds) and turned-off (from 120 – 360 seconds). Consider for 0 – 10% CZO, it was found that the more mol% of Cu, the higher the temperature on glass surface. However, with excess of %Cu (15 – 25% Cu), the surface temperature reduced from that of 10% CZO. Nevertheless 15% CZO had the best IR insulation property which will be described next as to why it is so. Series of thermal photographs of 15% CZO taken every 30 seconds obtained from the IR camera were shown in figure 7. Similar thermal insulation experiments like in figure 7 were conducted for all samples. Data from figure 7 were used to plot figure 6.

Results from the in-lab set-up to mimic a house with a glass window, set-up shown in figure 2, the average temperatures at T2, T3 and T4 were plotted in a bar graph in figure 8. Considering 0 – 10% CZO, it indicated that the more mol% Cu, the higher temperature at T2. Hence 10% CZO displays the highest temperature at T2 (88.8°C) and the lowest temperatures at T3 (51.8°C) and T4 (41.1°C). This implied that 10% CZO was suitable to block the transmission of IR rays than 0 – 5% CZO. The higher temperature at T2 means a better reflectivity to the IR rays which is proper for Low-E glass application since IR rays cannot pass through the coated glass. Although the surface of coated glass of commercial
ATO showed the highest temperature (94.9°C), the temperature inside the box (T3 and T4) was still higher than of 10% CZO. This is due to the NIR absorption property ATO. ATO absorbs the IR radiation on the outer surface (T2) and the accumulated heat is transferred into the box. Conversely, 10% CZO reflected IR radiation causing the temperature at T2 to increase, however the heat is not cumulated in the coated glass and is not transferred to the interior of the box resulting in a lower T3 compare to ATO.

Figure 4. SEM micrographs of undoped and doped ZnO with 0 – 25 mol% Cu at different magnifications.

For 15 – 25% CZO, with n-ZnO and p-CuO (a nano p-n junction), 15% CZO was most suitable as heat insulation with large uniform shape and particle size, and the high %reflection of the NIR region,
and the lowest temperature for T3 and T4. It is to be noted that the temperature difference (figure 8) for the different samples were rather small, this is because our coated glass slide covered only ~5% of the total exposure area. A more significant difference is expected with larger area of the coated glass or windows.

**Figure 5.** UV-Vis-NIR spectra in reflection mode.

**Figure 6.** Plot of the temperatures on the coated glass slide when the IR lamp was turned-on and turned-off.

**Figure 7.** Thermal photographs of 15% CZO obtained from IR camera at different times.

### 4. Conclusions

Copper-doped zinc oxide (CZO) was successfully prepared from Zn(CH$_3$COO)$_2$·2H$_2$O and Cu(CH$_3$COO)$_2$·2H$_2$O with MEA and isopropanol as a stabilizer and solvent, respectively. To obtain the CZO powder the solution was calcined at 550°C for 3 hours. CZO powder was confirmed by XRD spectra and found that 1 – 5 mol% Cu does not change the ZnO structure. All of samples still have a high degree of crystallinity with a hexagonal wurtzite structure. When mol% of Cu was higher than 5%, the excess Cu ions formed CuO as shown in the XRD spectra. Because the solubility limit of Cu ions in ZnO structure was 5%, the morphology of CZO was the same as undoped ZnO. However, with excess Cu ions, 15 – 25 mol% CZO, the nanoparticles exhibit larger particle size.

The emissivity of each sample were examined by the IR thermal camera. For 0 – 10% CZO, increasing mol% of Cu can promote the IR reflective property of CZO. High IR reflective characteristic of CZO lead to high temperature on outer glass surface (T2). From the emissivity experiment, it proved that 10% CZO was the best sample as an insulation material. The emissivity results were consistent with the thermal insulation experiment because the lowest temperature at T3 and T4 were also from 10% CZO.
On the other hand, for 15 – 25% CZO synergistic effect of n-ZnO and p-CuO, 15% CZO yielded the most appropriate mol% Cu with the lowest temperature inside the insulation box (T3). Notwithstanding this synergistic effect of 15% CZO had more influence than the heat reflection of 10% CZO. The 15% CZO is a better heat insulator than 10% CZO. UV-Vis-NIR spectra indicated that 15% CZO had the highest % reflection of IR region and reflects lesser of visible spectrum which is a bonus for the material in transparent coating application. Finally, the addition of Cu impurity to ZnO can improve ZnO property, i.e. reducing % reflection in visible region and promote IR insulation property.

![Graphs showing temperature distribution](image)

**Figure 8.** Bar graphs of the average temperature at (a) T2 (b) T3 and (c) T4 while the IR lamp was turned-on with the average source temperature of ~70°C.

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