

# Synthesis and optical characterization of C-SiO<sub>2</sub> and C-NiO sol-gel composite films for use as selective solar absorbers

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## ABSTRACT

We present a cheaper and environmentally friendly method to fabricate efficient spectrally selective solar absorber materials. The sol-gel technique was used to fabricate carbon-silica (C-SiO<sub>2</sub>) and carbon-nickel oxide (C-NiO) composite films on aluminium substrates. UV-Vis and FTIR spectrophotometers were used to determine the solar absorptance and thermal emittance of the coatings. C-NiO coatings gave the best spectral characteristics. We show that it is possible to achieve a solar absorptance of 0.94 and a thermal emittance of 0.12. So far, to our knowledge, no commercial spectral solar absorber has these spectral responses.

**Keywords:** Spectrally selective solar absorbers, solar absorptance, thermal emittance

## 1. INTRODUCTION

There has been an increasing demand for spectrally selective solar absorbers over the last few decades due to the energy crisis facing the whole world. Scientists and engineers throughout the world are working on ways to improve existing solar absorbers in order to harness solar energy effectively. These ways include finding appropriate coating materials and substrates to form what are called absorber-reflector tandem solar absorbers [1]. The best substrate currently in use is aluminium [2, 3] because of its high reflectance in the IR wavelength range. The struggle now is to find the appropriate material to coat the Al substrates to improve the absorptance. NiO has been found to have good absorptance properties in the visible region [4]. An ideal selective solar absorber has 100 % absorptance in the UV-Vis-NIR spectrum (0.3 – 2.5 μm) and 0 % emittance in the near- to far-IR (2.5 – 50 μm) spectrum. Addition of carbon is being proposed in this work in order to further increase the absorptance of NiO [5].

## 2. THEORETICAL CONSIDERATIONS

### 2.1 Solar and thermal radiation energy

The sun is the provider of nearly all of the energy on the earth. The total intensity of solar radiation falling on the earth is the sum of the direct radiation, diffuse radiation and reflected radiation. Fig 2.1 shows the solar hemispherical spectral irradiance for air mass 1.5 (ISO 9845-1, 1992 [6]) and the blackbody spectral emittance at different temperatures.

It is well known that all objects above absolute zero temperature emit thermal radiation whose wavelength and intensity depends on the temperature and optical properties of the body. A blackbody is an ideal body that absorbs all wavelengths of the incident radiation and emits the maximum amount of energy according to Plank's law [7]. Plank's law of blackbody radiation gives the spectral intensity,  $E_{\lambda b}$  of electromagnetic radiation from a blackbody at temperature,  $T$  as:

$$E_{\lambda b} = \frac{2\pi hc^2}{\lambda^5} \left[ \frac{1}{e^{hc/\lambda kT} - 1} \right] \quad (1)$$

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where  $E_{\lambda b}$ , the spectral intensity is in  $\text{W m}^{-3} \text{sr}^{-1}$ ,  $h$  is the Plank's constant in  $\text{J s}^{-1}$ ,  $c$  is the speed of light in vacuum in  $\text{m s}^{-1}$ ,  $\lambda$  is the wavelength of the radiation in meters and  $k$  is the Boltzmann constant. The total energy  $E_{\lambda}$  emitted from the blackbody is given by the Stefan-Boltzmann law:

$$E_b = \int_0^{\infty} E_{\lambda b} d\lambda = \sigma T^4 \quad (2)$$

where  $\sigma$  is the Stephan-Boltzmann constant.

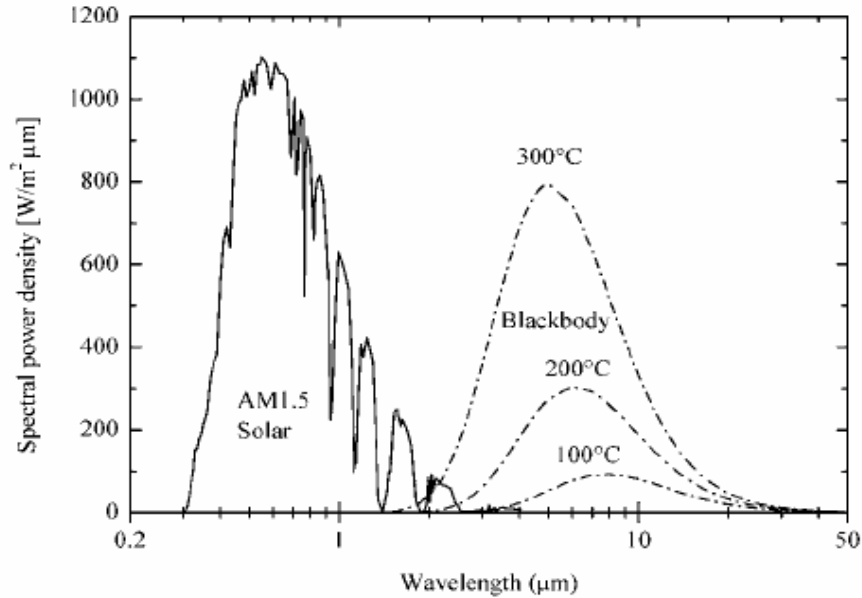


Fig 1. Solar hemispherical spectral irradiance for air mass 1.5 (ISO 9845-1, 1992) and blackbody spectral emittance at 100°C, 200°C and 300°C.

## 2.2 Solar absorptance and thermal emittance

For near normal spectral reflectance measurements, the solar absorptance,  $\alpha_{sol}$ , is defined as the ratio of the absorbed radiation to that incident on the surface [6]:

$$\alpha_{sol} = \frac{\int_{0.3}^{2.5} I_{sol}(\lambda)(1-R(\lambda)) d\lambda}{\int_{0.3}^{2.5} I_{sol}(\lambda) d\lambda} \quad (3)$$

where  $R(\lambda)$  is the spectral reflectance of the surface and  $I_{sol}(\lambda)$  is the solar spectral irradiance.  $I_{sol}(\lambda)$  is defined by the ISO standard 9845-1 (1992) for air mass (AM) 1.5. The thermal emittance is defined in the same way against the spectral blackbody radiation  $\rho(\lambda)$  at 100°C as:

$$\epsilon_{therm} = \frac{\int_{2.5}^{20} \rho(\lambda)(1-R(\lambda)) d\lambda}{\int_{2.5}^{20} \rho(\lambda) d\lambda} \quad (4)$$

Equations (3) and (4) were used to compute the values of  $\alpha_{sol}$  and  $\epsilon_{therm}$  from the reflectance spectra of the samples.

### 3. SAMPLE PREPARATION AND OPTICAL MEASUREMENTS

#### 3.1 Substrate preparation

All coatings were done on rough aluminium substrates. Flat aluminium sheets were cut into square shapes measuring 55 mm by 55 mm. The substrates were pre-washed before being treated in an acid bath. The pre-cleaning involved washing the substrates in aqueous detergent to remove grease particles. The pre-cleaned substrates were thoroughly rinsed and put in a phosphoric acid ultrasonic bath at 60 °C for about 45 minutes to remove the protective oxide layer. They were then thoroughly rinsed using distilled water to remove the acid. Finally they were dried slowly using a hot plate stove and coated within a few minutes to avoid re-contamination.

#### 3.2 C-NiO sol preparation

The following materials were used: 100 ml plastic bottles, sucrose (SUC), distilled water, nickel acetate ( $M=248.84\text{g/mole}$ ,  $(\text{CH}_3\text{COO})_2\text{Ni}\cdot 4\text{H}_2\text{O}$ , AR) as precursor, diethanolamine ( $M = 105.14\text{ g/mol}$ ,  $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$ , DEA, AR) as chelating agent, ethanol ( $M = 46.07\text{ g/mol}$ ,  $\text{CH}_3\text{CH}_2\text{OH}$ , EtOH, AR) as solvent and polyethylene ( $M = 2000\text{ g/mol}$ ,  $\text{H}(\text{OCH}_2\text{CH}_2)_n$ , PEG, AR) as organic template. 0.03 moles of nickel acetate were added to 50 ml of ethanol. The solution was stirred for 1 hour using a magnetic stirrer to dissolve all nickel acetate. 0.06 moles of DEA were added to the solution. Stirring continued for 5 minutes. PEG was added to the solution and stirring continued for 5 minutes to make sure that there was complete mixing. Finally sucrose was added to the mixture. The sol was ready for deposition after 1 minute of stirring. The above procedure was repeated with varying amounts of PEG and SUC taking care to change the composition of only one ingredient at a time.

#### 3.3 C-SiO<sub>2</sub> sol preparation

The following materials were used: distilled water, SUC, hydrochloric acid (HCl), tetraethyl orthosilicate ( $M = 208.33\text{ g/mole}$ ,  $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$ , TEOS, AR) and methyl trimethoxysilane ( $M = 178.3\text{ g/mole}$ ,  $\text{Si}(\text{OCH}_2\text{CH}_3)_3\text{CH}_3$ , MTES, AR). 100 ml of distilled water were put into a plastic bottle. Drops of HCL were added while stirring until the pH was 2. Six grams of SUC were added to 9 g of the acidified solution and the solution stirred until all SUC had dissolved. 12 g of TEOS were then added and the solution stirred for 5 minutes. Finally 2.4 g of MTES were added to the solution. Stirring was done for 12 hours before the sol was ready for deposition.

#### 3.4 Spin coating of substrates

The prepared sols were used in coating aluminium substrates using a P-6708D 8" desktop precision spin coating system. The spin coater was programmed such that it could rotate at the coating speed for 20 minutes. The dispensing of the sol was done uniformly using a 2 ml syringe once the coating speed was reached. The amount of sol dispensed was fixed at 2 ml to make sure that the thickness of the coatings was uniform.

#### 3.5 Heat treatment of coated substrates

After coating, the samples were put into a tube furnace for carbonization. The furnace temperature was raised to the desired temperature at a rate of  $5\text{ }^\circ\text{C min}^{-1}$ , maintained at that temperature for 60 minutes and then cooled to  $25\text{ }^\circ\text{C}$  at a rate of  $20\text{ }^\circ\text{C min}^{-1}$ . Nitrogen gas was continuously pumped into the furnace throughout the carbonization process to maintain an inert atmosphere.

#### 3.6 Optical characterization

UV/Vis/NIR measurements were done using a Shimadzu LISR-3100 spectrophotometer. The angle of incidence in this instrument was fixed at  $7^\circ$ . A  $\text{BaSO}_4$  standard white plate was used for baseline corrections. IR measurements were done using the Buck M500 IR spectrophotometer without an integrating sphere. Baseline corrections were done using a mirror in the sample position. All scans were converted to percentage reflectance spectra.

Data points obtained from the two instruments were combined to give a complete UV – IR spectra. Calculations of absorptance and emittance were done using a Matlab program that incorporated equations (3) and (4). The limits were  $\lambda_1 = 0.3 \mu\text{m}$  and  $\lambda_2 = 2.5 \mu\text{m}$  for the solar absorptance and  $\lambda_1 = 2.5 \mu\text{m}$  and  $\lambda_2 = 20 \mu\text{m}$  for the thermal emittance.

#### 4. RESULTS AND DISCUSSION

Two types of materials were investigated in this work. These are carbon in silica (C-SiO<sub>2</sub>) and carbon in nickel oxide (C-NiO). It was easy to combine spectra from the two instruments. Slight differences occurred due to the fact that the M500 IR spectrophotometer did not have an integrating sphere. Some of the results obtained in this investigation are presented below.

##### 4.1 Effect of SUC composition on C-NiO samples

Fig 2 shows the effect of adding SUC on the NiO. The shape of the spectra clearly shows that two regions exist. As is expected of a good solar absorber, the reflectance in the solar spectral range (0.3 to 2.5  $\mu\text{m}$ ) is below 50 % and that in the IR (above 2.5  $\mu\text{m}$ ) range is above 50% for a greater number of samples. Samples with 12 g SUC had the least reflectance whilst those with 7 g SUC had the highest reflectance. Some samples with SUC had higher reflectance values than those for sample without SUC. We expected sample without SUC to have the highest reflectance and therefore the least absorptance. The only reasonable explanation to this unexpected behavior could be the fact that there were chemical reactions that took place when the samples were heated at temperatures as high as 500 °C. We suspect that a reduction reaction took place between the carbon and NiO. This reaction reduced the amount of Carbon and NiO on the samples.

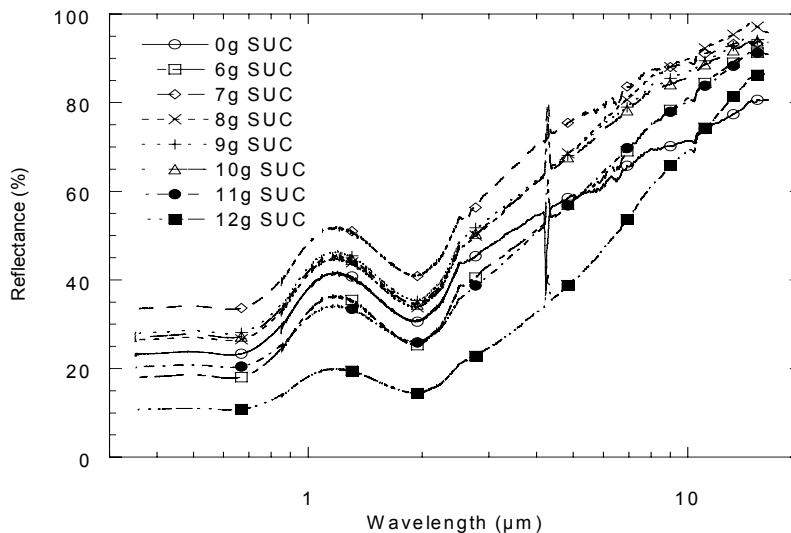


Fig 2. Effect of SUC composition in C-NiO samples.

In the IR range, the reflectance increases gradually and uniformly for all samples except for the sample without SUC which increases at a slower rate. The Reflectance of samples with low SUC content is higher than that for samples with higher SUC content. This behavior was also observed by Katumba et al [1]. The explanation given to this was that samples with high SUC content are thicker than samples with low SUC spin coated at the same speed. An increase in SUC content increases the viscosity of the sols. It is general knowledge that more viscous sols do not spread easily during spin coating. The optimum SUC content for samples with high absorptance and low emittance was 8 g. There was another advantage for choosing samples with a SUC content of 8 g. This was the time it took for the sols to remain suitable for coating after they had been prepared. Sols deteriorated and turned into suspensions after adding SUC. Sols with 8 g SUC stayed longer than samples with more SUC which gave us enough time to do the coating.

## 4.2 Effect of PEG composition on C-NiO samples

Fig 3 shows the effect of the composition of PEG on C-NiO samples. The reflectance values are spread much in the solar spectral range but seem to merge in the far-IR range. Samples without PEG had lower reflectance in the solar spectral range. The reflectance increased as the composition of PEG was increased. It peaks for samples with 1 g of PEG and then starts to decrease. In the IR region, the reflectance of the sample without PEG rose faster than that for other samples. These observations point to the fact that addition of PEG affects the solar absorptance more than it affects the thermal emittance of the samples. A research done by Zhifeng et al. show that films without PEG are compact; they become porous with the addition of correct amounts of PEG. Our results therefore suggest that compact films (no PEG) have lower reflectance in the solar spectral range hence higher absorptance than porous films. In order to have slightly porous films with good spectral properties we chose an optimum PEG content of 1.0 g. This was fixed throughout this research.

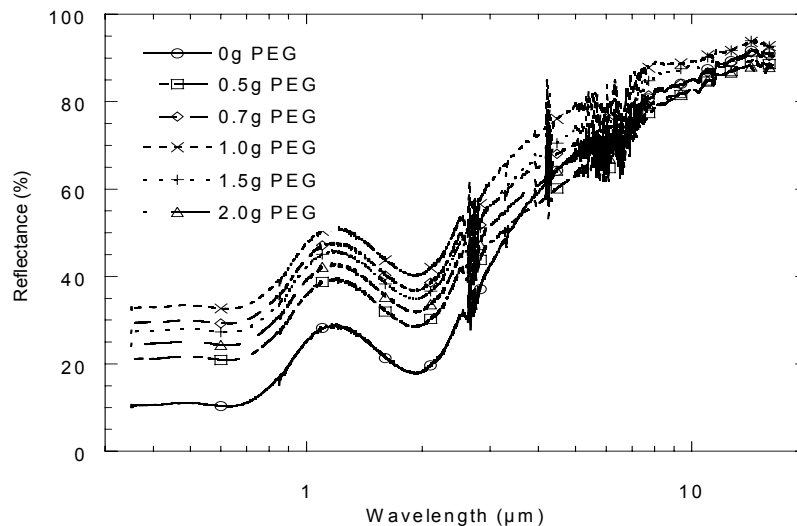


Fig 3. Effect of PEG composition in C-NiO samples

## 4.3 Effect of spin coating speed on C-NiO samples

Fig 4 shows the effect of spin coating speed on C-NiO samples. For wavelengths less than 2.5 μm, the reflectance decreased with spin coating speed. This is in agreement with theory that suggests that the higher the spin coating speed the thinner the film and hence the lower the absorptance. A possible explanation to this is that the amount of NiO decreases with spin coating speed and as a result the reduction reaction is slowed down. Thinner samples therefore have more carbon than thicker samples. The higher reflectance of samples spin coated at lower speeds is an indication that those samples have more NiO. An optimum speed was obtained by calculating the  $\alpha_{sol}/\epsilon_{therm}$  ratio. The speed that had the highest  $\alpha_{sol}/\epsilon_{therm}$  was considered to be the optimum and a value of 3000 rpm was identified and used for the rest of the experiments.

## 4.4 Effect of heat-treatment temperature on C-NiO samples

Fig 5 shows the variation of reflection with heat treatment temperature of C-NiO samples. Samples heat-treated at 300 °C and 500 °C have the lowest reflectance in the region of lower wavelengths up to about 8 μm. The reflectance values were highest for samples heat treated at 400 °C. The reflectance spectra for all samples merged at higher wavelengths. This suggests that the temperature at which samples are heat treated has a greater effect on the solar absorptance of the samples than on their thermal emittance. This is expected since the heat-treatment temperature only affects the amount of carbon in the samples.

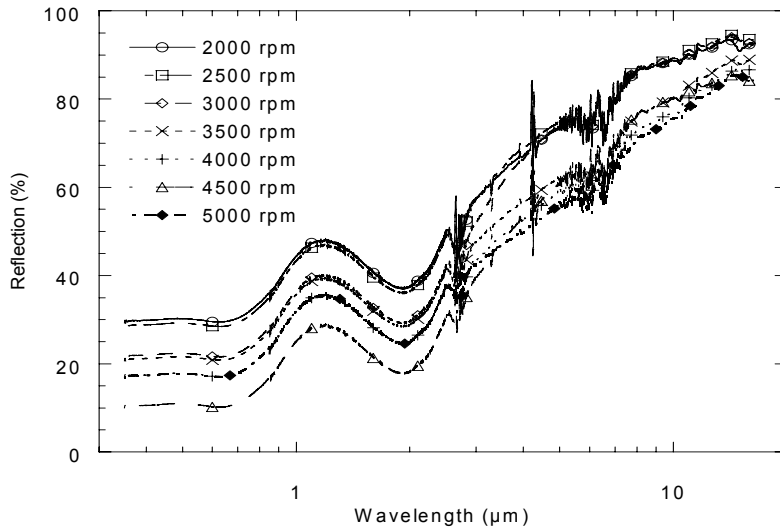


Fig 4. Effect of spin coating speed on C-NiO samples.

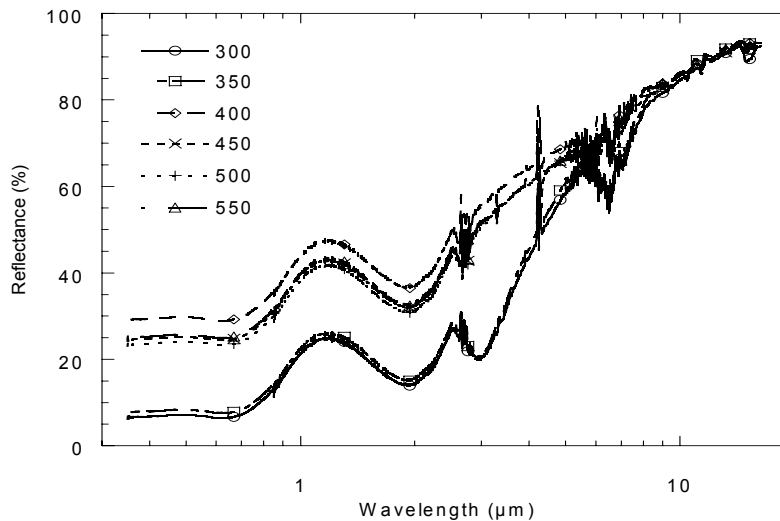


Fig 5. Effect of heat-treatment temperature on C-NiO samples.

As the temperature is raised the carbon starts to react with NiO resulting in the low absorbance of the samples. Ni which is a by-product in this reduction reaction resembles a solar absorber itself and so does not have any observable effect on the spectral properties of the samples. The temperature that had the highest  $\alpha_{sol} / \epsilon_{therm}$  ratio was 350 °C. This is the temperature just before the amount of carbon starts to decrease due to the reduction reaction.

#### 4.5 Effect of heat-treatment temperature on C-SiO<sub>2</sub> samples

Fig 6 shows how the reflectance of C-SiO<sub>2</sub> samples increases with heat treatment temperature. Samples heat-treated at 300 °C and 400 °C had the lowest reflectance and samples heat-treated at 550 °C had the highest reflectance. One would expect the reflectance of the samples to decrease with temperature since the carbon concentration is expected to increase as the film thickness decreases. The transition from low reflectance to high reflectance occurs at a wavelength of about 3 μm. It shifts towards shorter wavelengths as the heat treatment temperature is increased. No noticeable change of order occurs in the IR region except that the samples heat treated at 500 °C now have the highest reflectance. The

optimum temperature for heat-treatment of C-NiO samples was chosen as 500 °C. Generally the reflectance of C-SiO<sub>2</sub> samples is very low. The reason for this is that the samples developed many cracks even though MTES was added to reduce them. This meant that the reflectance of the SiO<sub>2</sub> was more of diffuse than specular. Reflectance measurements of such samples require spectrophotometers with integrating spheres.

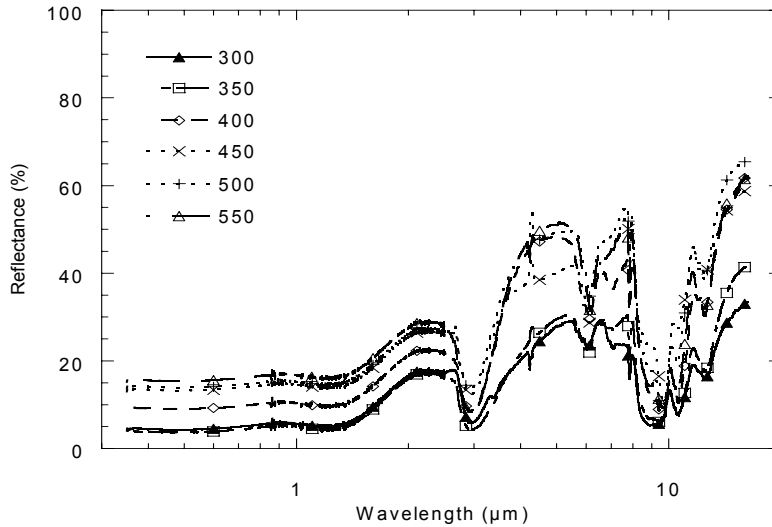


Fig 6. Effect of heat-treatment temperature on C-SiO<sub>2</sub> samples

#### 4.6 Limits of absorptance and emittance

Fig 7 shows various combinations of solar absorptance and thermal emittance values for the C-NiO and C-SiO<sub>2</sub> samples used in this investigation.

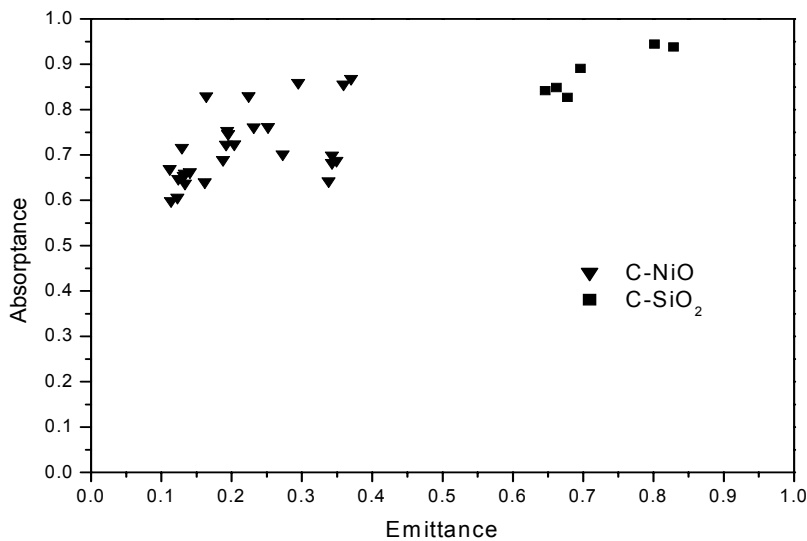


Fig 7. Scatter graph of absorptance and emittance values for C-NiO and C-SiO<sub>2</sub> samples used in this investigation.

From the graph, it can be seen that C-NiO has more promising results than C-SiO<sub>2</sub>. The optimum figures achieved in a single sample for C-NiO were 0.63 and 0.11 for absorptance and emittance respectively. The limit for absorptance is about 0.94 and that for emittance is about 0.12. Absorptance and emittance values obtained in this investigation

compare very well with what was reported by Kennedy [4]. Kennedy's report shows that absorptance and emittance values for Ni<sub>x</sub>-NiO solar absorbers obtained so far are 0.96 and 0.10 respectively. C-NiO absorbers have a greater potential of overtaking most commercial solar absorbers currently in use.

## 5. CONCLUSIONS

This work has demonstrated that it is possible to fabricate low cost C-NiO selective solar absorbers using readily available materials by the sol-gel process. The optimum SUC content was chosen as 8 g. Measurements showed that the addition of PEG is not welcome since it worsens the optical characteristics of C-NiO samples. A small amount of PEG was required to make the samples porous. The absorptance was found to increase with spin coating speed. The optimum spin coating speed was chosen as 3000 rpm. The solar absorptance of C-NiO samples was found to be affected by high heat-treatment temperatures. A reduction reaction which reduced the amount of carbon took place. Further investigation into this is required before the C-NiO solar absorbers can be commercialized. The optimum temperature was chosen as 350 °C. C-SiO<sub>2</sub> samples showed poor optical properties. The reason being that their reflectance was found to be rather diffuse than specular. A spectrophotometer with an integrating sphere is therefore required to make measurements on such samples. The optimum temperature for C-SiO<sub>2</sub> samples was found to be higher than that for C-NiO samples. It was found to be 500 °C.

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