A review of near infrared reflectance properties of metal oxide nanostructures

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ABSTRACT

The light that reaches the Earth's surface ranges over a broad spectrum of wavelengths (295 – 2500 nm): ultraviolet (UV) radiation that you can't see or feel, visible light that you see, and infrared radiation that you feel as heat. Almost half of the sun's energy is from infrared and near infrared radiation. However, these radiations on absorption result in heating up of the surface. Significant amount of heat is absorbed into the surface by means of conduction. With such increasing heat, there is a need for variable energy in the form of air-conditioning to keep the interiors of the building cool for people to work and live inside. To reduce the increasing demand for energy consumption for air conditioning, there is a need for cooler roofs. Reflecting the sun's radiation minimizes the amount of energy absorbed by the building.

A cool coating reflects a high percentage of incident near infrared (NIR) radiation, while transmitting high levels in the visible spectra. This will reduce the amount of solar energy entering buildings which results on a cool surface when exposed to the sun. In hot summer time, cool coatings will help to keep the roof temperature down, minimizing the energy required to keep homes and buildings maintained at a comfortable temperature.

NIR reflective pigments have been used in military, construction, plastic, and ink industries. A particular class of such pigment is based on mixed metal oxides. Recently, the NIR reflective pigment with nanocrystalline metal oxides has shown remarkable NIR reflectance with better colour choices.

In this report, studies devoted to the preparation of cool paint with NIR reflectance properties of metal oxides have been reviewed. The NIR reflectance of metal oxide nanostructures (such as TiO_2 and ZnO) synthesized in-house has also been studied and presented in this report.

Powders of TiO_2 and ZnO nanostructures were synthesized using an arc discharge method with in-house apparatus at GNS Science. Morphology analyses revealed that both TiO_2 and ZnO have nano sized structures and the arc discharge current has an effect on the structure size. TiO_2 nanostructures synthesized at 74 A arc current show diffuse reflectance from 49 % to 45 % in the NIR range (700 – 2500 nm). ZnO nanostructures show diffuse reflectance from 57 % to 14 % in the NIR range (700 – 2500 nm).

KEYWORDS

Near infrared reflection, cool paint, metal oxide, TiO_2, ZnO

1.0 INTRODUCTION

Light energy from the sun spans a wide range of wavelengths. Only small portion of the total energy reaches the Earth's surface which ranges from 295 – 2500 nm in wavelength.

- Ultraviolet (UV) region (295 - 400 nm): UV light is a form of radiation which is not visible to the human eyes. It's in an invisible part of the "electromagnetic spectrum". It affects human health both positively and negatively. Short exposure to UVB radiation (wavelength: 290-320 nm) generates vitamin D but can also lead to sunburn. UV accounts for about 5 % of the sun's energy and degrades the binder of the coatings.
- Visible region (400 - 700 nm): Visible light waves are the only electromagnetic waves human beings can see. We see these waves as the colors of the rainbow. Each color has a different wavelength. Around 50 % of the sun's energy occurs in this region. Pigment selectively absorb the visible light and reflect the remaining. Thus the visible region consists of wavelengths that give us the perception of colour.
- Near infrared (NIR) region (700 - 2500 nm): NIR light has wavelengths that are longer than those of visible light, meaning that humans can't see it. 45 % of the total solar energy is in the infrared radiation region. The heat-producing region of the infrared radiations ranges from 700 – 1100 nm, which results in heating of the surface if absorbed.

NIR reflective pigments can be overall classified as inorganic and organic pigments. They reflect wavelengths in the infrared region and reflect some visible light selectively. The reflectivity and absorptivity of the pigment are in dependent of each other, which makes the NIR reflective with colour. The inorganic class of NIR reflective pigments are mainly metal oxides and they are increasingly used for roof and building coatings because of their excellent weather abilities and high heat stabilities. They have the ability to maximize reflectivity in the NIR region. These pigments are highly stable and chemically inert. They can withstand chemically aggressive environments and still retain their colour. Formulating paints with NIR reflective pigments is a major challenge since the binders degrade much faster.

General benefits of NIR reflective coatings are summarized:

- Reduction of the "Urban heat island effect".
- Reduction in air pollution because of low energy usage, power plant emissions and reductions in urban air temperatures.
- Lowering energy demand for air conditioning, particularly in equatorial regions.
- Longer life-cycle because of less polymer degradation and thermal expansion from lower temperature.
- Improvement of system durability and less thermal degradation.
- Cooler to touch for better handling.
- Aesthetically pleasing colours.

2.0 REFLECTION MECHANISM OF INFRARED RADIATIONS

2.1 LIGHT REFLECTION

Absorption of light occurs when light energy promotes electrons from one bonding state to another. If light of a different wavelength is used to cause this energy transition, it will not be absorbed. This means there are electronic transitions responsible for absorbing light with wavelengths of energy from 400-700 nm. Light of lower energy (> 700 nm) is not absorbed. In this case, a beam of light with a wavelength of 1500 nm is too low in energy to cause any electronic transitions in the material. Thus it will not be absorbed. Instead the 1500 nm light beam is refracted, reflected and scattered, leading to the diffuse reflection of NIR light. There is no method to predict the NIR reflectivity of an inorganic or organic compound.

When a beam of light falls on a powdered sample, reflection, transmission, and absorption can occur. If the sample is optically thick enough, the transmitted light is negligible. There are two types of reflection: specular reflection and diffuse reflection. Specular reflection is significant for optically smooth surfaces and for highly absorbing samples. Diffuse reflection occurs when the incident radiation penetrates into the powder and gets reflected by grain boundaries of the particles. Diffusion reflection depends on particle size and when the particle size decreases, the number of reflections at the grain boundaries increases. As a result, the depth of penetration of incident light decreases leading to a decrease in absorption and increase in reflectance. The net effect will be a decrease in the absorbed portion of light and an increase in the reflected portion of light.

Reflective pigments can be:

- Pure metals, such as Al, Ag and Cu
- Metals with surface coatings (AlO(OH) on Al and AgS on Ag)
- Multiple-layered structures: TiO_2/Au/TiO_2, Silicon powder and metal coated cenosphere particles

Coated metals have been used to decrease the reflectance of visual light. For example, the coating outside of the metal, which can be considered as a metal oxide, will absorb visual light, while IR light of a longer wavelength will pass through the coating and be reflected by the underlying metal [1].

The multiple-layered structures are designed to minimise the reflection of visual light while giving a high reflection of IR light. The physical principle is destructive and constructive interferences of light from differences in refractive indexes between combinations of quarter wavelength thin layers of metals or dielectrics (as shown in Figure 1.). A multiple-layer structure was fabricated by sputtering on a PMMA substrate and divided into flakes when removed from the substrates after being sputtered [2]. Si transmits light well in the IR range, except for around 10 µm where Si-O absorbs most of the radiation. When IR radiation falls on Si powder, light which transmits through the Si grains will be reflected at each Si-air boundary (or Si-binder boundary in a paint). This will cause a strong backscattering effect, resulting in high reflectance. The higher the difference in refractive index between the particle and surrounding medium, the stronger the backscattered power will be.

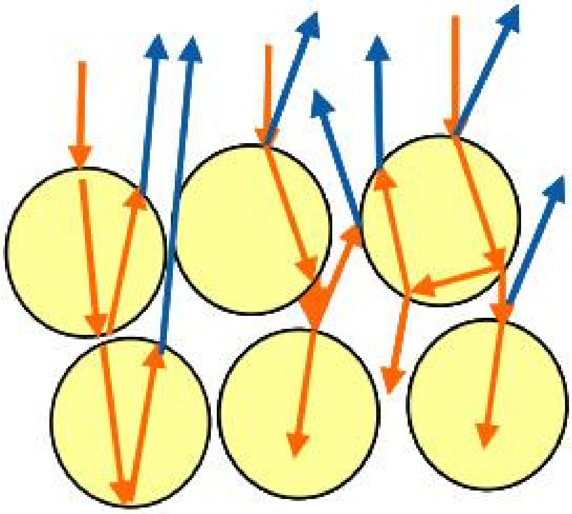

Figure 1 Principle of backscattered reflectance for transmitting particles.

2.2 FACTORS AFFECTING INFRARED REFLECTIVITY

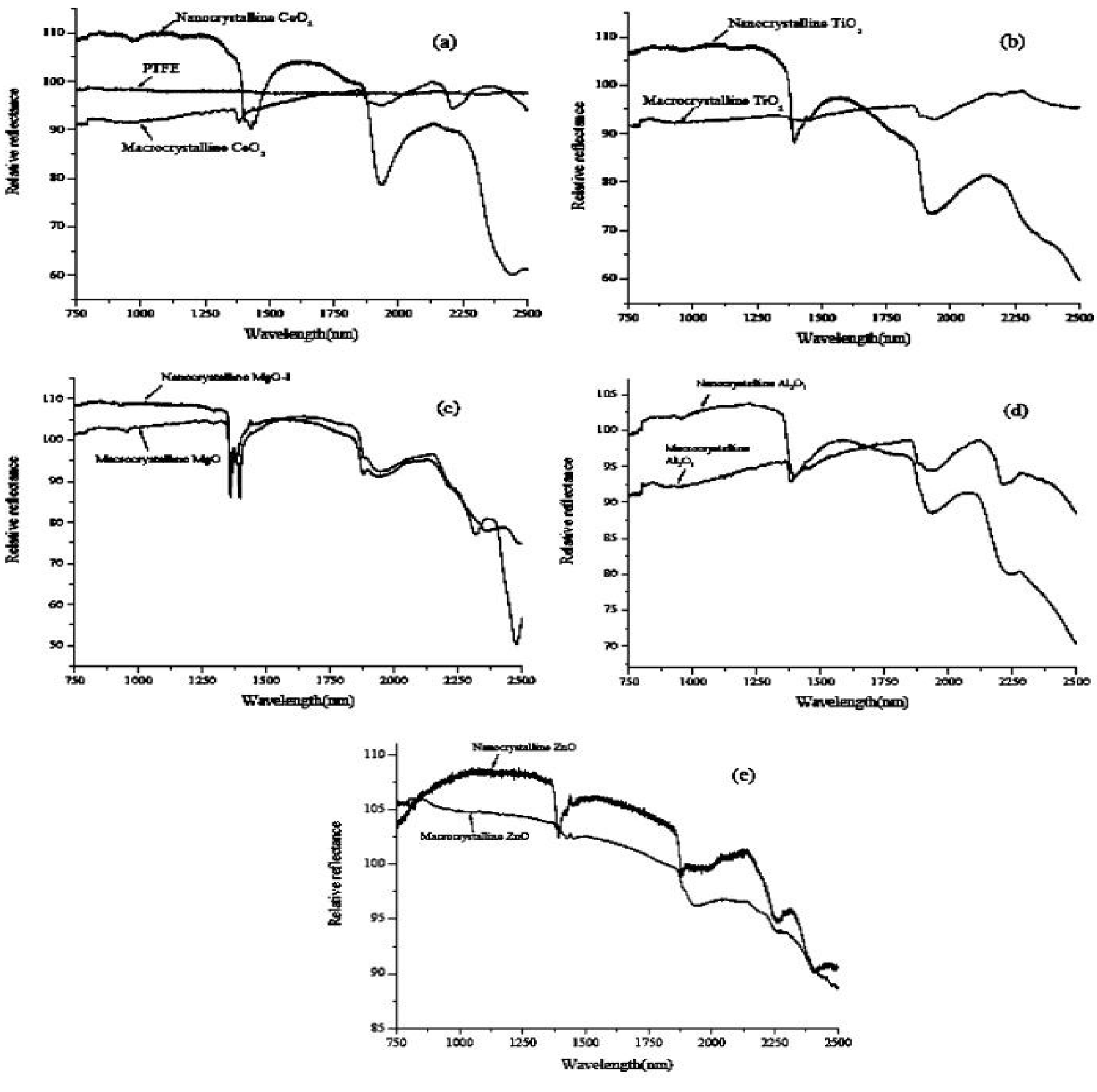

Figure 2 Near-infrared reflectance spectra of nanocrystalline metal oxides and macrocrystalline metal oxides; the reflectance of PTFE (reference) is about 100 [3].

Paint is a fine dispersion of pigments in binder(s) in the presence of solvent(s) and a small amount of additives. The final properties of the paint or coating depend on the properties of the binder, pigments and additives. Many other ingredients or additives in the paint, such as, solvent (water), thickener, coalescent, dispersing agent, antifoaming agent, extender, anticorrosion agent, and different colour pigments for the visual colour, will improve various properties of the paint. Pigments alter the appearance of the coating by selective absorption or by scattering of light. The important physical-optical properties of pigments are their light-absorption and light-scattering properties. If absorption is very small compared with scattering, the pigment is a white pigment. If absorption is much higher than scattering over the entire visible region, the pigment is a black pigment.

NIR reflectivity depends on the relative refractive index of the particles and that of their surrounding medium, distribution of particles in the coating, loading of particles, binder concentration and wavelength of the incident light.

The important physical data for inorganic pigments comprise not only optical constants, but also geometric data: mean particle size, particle size distribution, and particle shape [4]. Particle size of the pigment is a very important parameter affecting NIR reflectivity. Pigment containing nanoparticles significantly enhances the reflective properties. For the highest reflectivity, the particle size should be more than half the wavelength of the light to be reflected. Thus for reflecting infrared light of 800-1200 nm wavelength, particle size should be at least 0.4 to 0.6 microns.

Figure 2 shows the results of the reflectance measurements on the nanocrystalline metal oxides (CeO_2, TiO_2, MgO, Al_2O_3, and ZnO) in the region 750 - 2500 nm. The reflectance curves for the corresponding macrocrystalline oxides are also shown for comparison. A comparison between the NIR reflectance properties of nanocrystalline metal oxides and their macrocrystalline analogs show that the nanocrystalline metal oxides are more reflective compared to the bulk macrocrystalline oxides. Nanocrystalline CeO_2, nanocrystalline Al_2O_3, and nanocrystalline TiO_2 possess higher reflectance values (relative reflectance = 110, 102, and 108) compared to their bulk counterparts (relative reflectance= 92, 92, and 99). Also, nanocrystalline ZnO possesses about 5 % more reflectance in the region 980-1330 nm compared to the bulk ZnO [3].

Binder weight ratio affects the final reflectance of the coating. With the increase in the binder weight ratio, there is an increase in the diffuse reflectance of the coating. With higher binder weight ratio, there is a strong capillary action between the binder particles, causing them to fuse together and bind TiO_2 nanoparticles into a continuous film. It has been found that coating materials, with less than certain weight ratios are unable to form a stable coating layer and are easily detached from the plastic sheet. However, coatings with more than one certain weight ratio develop cracks which might be from the large surface tension of the coating.

Coating thickness is another factor which affects film reflectance. Higher coating thickness leads to better reflectance because of the higher number of nanoparticles on the substrate for reflecting.

The maximum diffuse reflectance, 97.12 -96.91 %, for a 0.25 mm thick coating with a 17 % pigment to binder weight ratio was obtained in which the crystallite size of TiO_2 is of 70.34 nm with particle size 170 nm.

2.3 THEORY OF LIGHT INTERACTION

Various theories describe the interactions of light include Mie theory and Kubelka-Munk (KM) theory. Mie theory is good for describing the interaction of light with spherical particles that are isolated and homogeneous. KM theory is widely accepted for explaining the optical properties of complex systems such as powders and inhomogeneous system.

According to KM theory

$$\frac{(1-R_{\infty})^2}{2R_{\infty}} = F(R) = K/S \tag{1}$$

where K is the absorption coefficient, S is the scattering coefficient, and R_{∞} is the reflectance of the sample at infinite thickness. F(R) is the KM function, also called the remission function. The reflectance of the sample depends on the ratio of K to S. When the particle size (d) decreases, the scattering coefficient (S) increases (for d ≥ 1 µm) resulting in a reflectance increase.

$$S \propto 1/d \tag{2}$$

When the particle size (d) increases, the depth of penetration increases and absorption increases, leading to a decrease in the reflectance.

Some previous studies on the NIR reflectance of different crystalline materials reveal that the NIR reflectance also depends on the mean particle size coupled with smaller crystalline size (as shown in Table 1). Usually reflectance increases with a decrease in mean particle size. The grain boundary of a particle consists of many crystallite faces. Because the crystallite size of nanocrystal is smaller than that for macrocrystalline materials, nanoparticles have more crystalline faces for reflecting the NIR light compared with the macrocrystalline materials.

Table 1 The effect of particle size on the NIR reflectance of nanocrystalline TiO_2 [3].

Size fraction	**710 µm-1.1 mm**	**710-425 µm**	**425-250 µm**	**250-180 µm**	**180-150 µm**	**< 150 µm**
Relative reflectance at 810 nm for nanocrystalline TiO2	76	94	96	96	102	106

It is recommended that if mean particle size is the only parameter used for determining the NIR reflectance, an oxide with the least mean particle size should be the most reflective. Because nanocrystalline TiO_2 possesses high refractive index (2.74) it is considered to be a promising candidate for NIR reflective pigments in the region from 750 to 1300 nm.

3.0 APPLICATIONS OF NIR REFLECTIVE PIGMENTS

NIR reflective pigments have been widely used in roof coatings, vinyl window and sliding, cement, concrete and pavers, and automotive applications. Apart from these applications, the NIR reflective pigments can also be used in domestic household applications such as military camouflage and infrared reflection from fire.

Fire-resistant paints have been formulated to reflect heat and to insulate from heat. They can keep the temperature of the coated combustible substrate below the ignition temperature. The US patent US5811180 describes the use of certain infrared reflective pigments in coating composition to enable the reflection of the fire radiation [5]. These NIR reflective coatings can be used on the surface of wood, polymers, fabrics and paper for reducing fire hazards and preventing substrate ignition. Non-combustible and painted metal containers for flammable liquids can be coated with such NIR reflective coating to keep the container surface cooler, and thus its flammable liquid contents cooler, when a fire is nearby.

Apart from roof coatings, NIR pigment can also been applied in window coatings. These coatings transmit the visible light and reflect the infrared light from the sun's radiations. Modern architectural designs employ the use of large glass areas. These contribute to the aesthetic appearance of the building, reduce maintenance and increase the energy consumption. Large glass surfaces in buildings account for large heat losses during the winter season and excessive heating by direct solar radiation in summer. The latter effect is a major contribution to energy cost since it costs three to six times more to cool a building than to heat it. Thin gold film has been verified to be a good candidate for window coating. However, because of the metallic glare and high cost of gold film, it is not a good commercial product for window coating. Haacke Gottfreid has used certain semiconductor metal layers as an alternative to heat reflective metallic films. He has stated that if the energy gap of these materials is large (approximately 3 eV), they are transparent to visible light. Also, if the free electron concentration in these semiconductors exceed to a large extent, these films also give high infrared reflectivity [6].

A few companies market NIR reflective pigments, for example, V-799 Cool Colors Black marketed by Ferro Corporation.

4.0 TiO_2 INFRARED REFLECTIVE PAINT PIGMENT

4.1 SIZE EFFECT

Recently, the optical properties of nanocrystalline and related materials have been of great theoretical and experimental interest. Nanocrystalline materials possess interesting optical properties such as increased band gap and enhanced fluorescence intensity. Among the nanocrystalline materials, metal oxide nanoparticles belong to an interesting class of compounds. Metal oxide nanocrystals can be prepared in unique shapes and they exhibit remarkably different chemical properties compared to macrocrystals. The particle size of an oxide can affect its colour that in turn can affect its reflectance properties. Moreover, metal oxide nanoparticles possess high surface areas making them useful for a variety of applications including coatings.

The naturally occurring oxides of titanium at atmospheric pressure exhibit three phases, anatase, brookite and rutile. The rutile phase is thermodynamically the most stable and possesses the highest density with a compact atomic structure. TiO_2 in the rutile phase is largely used as a reflective pigment in reflective coatings because of its effective light scattering properties. Coatings containing even small amount of rutile phase TiO_2 particles reflect almost the entire visible spectra. Reflective coatings of TiO_2 have been applied in commercial optical products such as optical fibers, scintillators, integrating spheres, luminaries, reflective panels and laser cavity mirrors.

Bulk TiO_2 particles of approximately 0.1 µm size are conventionally used as reflective pigments. These pigments are prepared by crushing the minerals obtained from their respective ores. After crushing, small granules are obtained. This results in individual particles of irregular shape, size and various compositions. To date, these materials have been used as reflective pigments and despite barely matching the requirements for reflective pigments.

Pigment materials containing nanoparticles significantly enhance the properties of various coatings, including scratch-resistance, UV protection and antibacterial property. Because of controlled morphology, high surface to volume ratio and high purity, TiO_2 nanoparticles are potential candidates for reflective pigments compared to their bulk counterpart. It was found that nano-TiO_2, especially in the rutile type, could reinforce the UV shielding ability of acrylic latex paint.

Of the available white pigments, the rutile phase of TiO_2 has the highest refractive index in the visible (2.7) and therefore has the strongest visible light scattering power at the optimum particle size of about 0.2 µm. Rutile TiO_2 is a direct bandgap semiconductor and therefore has a very abrupt transition from low absorption to high absorption that occurs at 400 nm, the boundary between the visible and UV regions.

The band gap energies ($\mathbf{E_g}$) of TiO_2 nanoparticles can be calculated using

$$E_g = \frac{hc}{r_{int}} \tag{3}$$

where h is Planck's constant (4.135 x 10^{-6} eV•nm), c the velocity of light (3 x 10^8 m/s), and, γ is the wavelength (nm) corresponding to the intersection of extension of linear parts of the spectrum of y-axis and x-axis. Increases in the crystallite size of rutile phase nanocrystalline TiO_2 leads to decreases in the energy band-gap values. It is well-known that the band gap of a semiconductor decreases with increasing crystallite size for TiO_2.

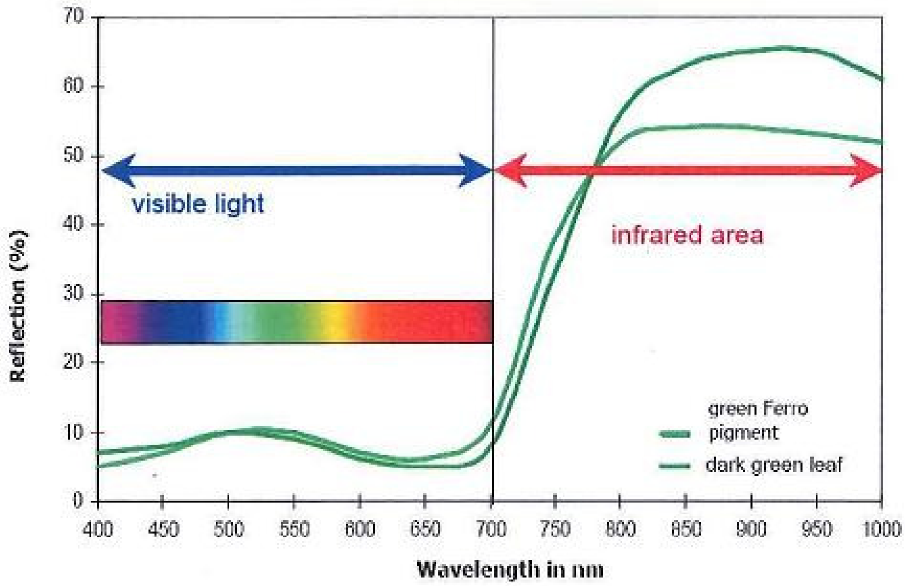

Figure 3 Reflectivity of green Ferro pigment compared with a chlorophyll curve. The green Ferro pigment shows an enhanced reflectivity of 50% in the NIR range.

The optimum TiO_2 particle size to produce a coating with reasonable temperature and moderate brightness was found to be 0.8 µm with brightness and temperature at 60.8 % and 60 $^{\circ}$C. When the size of TiO_2 particles changes from 0.2 um to 0.8 µm, the visible light reflectivity is reduced by approximately 25 %, while the NIR reflectivity increases by approximately 14 % [7].

In general, dispersed TiO_2 particles are sized at 1/3-1/2 of the wavelength of the incident radiation that is to be reflected, but their addition can change the colour, making a black more grey, for example. Several companies like Ferro and Shepherd Colour have formulated and patented specific IR reflecting pigment colours. Normally, dark pigments like carbon black have only about 6 % total solar reflectance. However, after mixing with metal oxides such as TiO_2, the IR reflecting black pigments can reach the 25-30 % total solar reflectance range. Figure 3 shows an example of green pigment from Ferro with enhanced reflectivity in the IR range.

Some IR reflective pigments (available from Ferro Corporation) were incorporated into a commercial automotive refinish basecoat composition. The IR reflective black, yellow and brown pigments were added to the basecoat at a total concentration of 22 % by weight of the dry film. Other pigments, such as TiO_2, were also added at a concentration of 22 % by weight of the dry film. The thermoplastic-polymeric binder system used to make the basecoat consisted of acrylic copolymers and cellulose acetate butyrate. The coatings were applied in a commercial body shop via standard spray techniques. The control basecoat contained conventional pigments, such as iron oxide, carbon black and TiO_2. The TiO_2 concentration in the control basecoat was the same as in the experimental basecoat. The visual colour was

approximately the same as the experimental basecoat. The binder systems in the two basecoats were the same, as were the compositions of the clear coats on both cases. Laboratory testing using a sum lamp yielded a 9 - 10 $^{\circ}$C difference in equilibrium panel temperature between experimental and control coatings. The measured solar absorptivities of the solar reflective and control coatings are 82 % and 89 %, respectively [8].

4.2 CHALLENGINGS FOR TiO_2 REFLECTIVE PAINT

TiO_2 is normally used for reflective “white” roof pigment. For years the vinyl siding industry has formulated different colours in the same polyvinyl chloride base by incorporating TiO_2 and black NIR-reflective paint pigments to produce dark siding that is cool. Researchers discovered that a dark colour is not necessarily dark in the infrared. Brady and Wake [9] found that 10 µm particles of TiO_2, when combined with colorants such as red and yellow iron oxides, phthalocyanine blue and paliogen black could be used to formulate fairly dark colours with NIR reflectance of 0.3 and higher.

Studies on the reflectance of TiO_2 particles have been the subject of significant research for many decades because their applications require high reflectance efficiency and photostability. The enhancement of photostability of rutile phase TiO_2 while maintaining reflectance at the same time has been a challenging subject. Recently, it has been found that rutile phase nanoparticles have higher absorption in the visible region compared to that of the anatase phase.

Doping TiO_2 with elements like Al, Li and K is one of the methods to improve the reflectance of TiO_2 particles. It creates defects in the TiO_2 crystal lattice and introduce traps for electrons and holes. This will prevent migration of electrons and holes towards the surface of TiO_2. The effect of Al doping on the reflective properties of TiO_2 nanoparticles, synthesized using the sol-gel method, has been investigated. It has been showed that with Al doping, the phase transition temperature for anatase to rutile phase increased; however, no change in morphology was observed. TiO_2 nanoparticles doped with 0.1 % Al show high photostability with no change in reflectance. The coating with Al doped TiO_2 nanoparticles has been applied on a plastic substrate with different coating thicknesses to design light reflectors. These reflectors have been found to have diffuse reflectance of 98.17 - 98.29 % for 0.25 mm thick coatings [10].

Current results show the enhancement of reflectance in the NIR range for doped TiO_2. Niobium (Nb)-doped TiO_2 films were synthesized using several different techniques adapted from the literature [11]. Nb was originally chosen as the dopant material because of its similarity in atomic radius to Ti^{4+} and the valence state it prefers. Other elements such as antimony, bismuth and vanadium are other candidates.

Table 2 Properties of several group V elements.

Element	Ionic Radius (Å)	Heat of vaporization (kJ/mol)
Niobium	0.70	690
Vanadium	0.59	453
Phosphorus	0.34	12.4
Arsenic	0.47	32.4
Antimony	0.62	68
Bismuth	0.74	160

If high reflectance is shown to be obtained by adding some dopant materials and annealing, methods other than heating can be explored to disperse the ions throughout the film.

5.0 OTHER TYPE OF INFRARED REFLECTIVE PIGMENT

Besides TiO_2, other types of semiconductor NIR pigments have been studied.

5.1 ZINC OXIDE

One of the most important applications of ZnO is in the paint industry as pigment. ZnO is a white powder that is usually used as pigment and by volume is the second most significant white pigment. Direct fabrication of special structures with controlled crystalline morphology represents significant challenge in various fields, because it can provide a better model for investigating the dependence of electronic and optical properties on the size confinement and dimensionality. Research has revealed that the optical properties of ZnO powders were strongly affected by the particle size and morphology. A significant improvement in the scattering efficiency of ZnO pigment can be obtained using an optimized nanostructured pigment [12].

The current state-of-the-art thermal control coating system for space assets uses a potassium silicate binder and ZnO pigment to maintain solar reflectance over a long exposure time. Results of modelling ZnO pigment embedded in a matrix similar to that of potassium silicate under solar irradiance conditions indicate that a narrow particle size distribution centered at 0.35 µm would provide the highest overall scattering coefficients, ranging from 0.75 μm^{-1} at 1000 nm to 5.0 μm^{-1} at 380 nm wavelengths. These results indicated that a significant improvement, 2 - 10 times dependent upon wavelength, in the scattering efficiency of ZnO-based thermal control coatings can be obtained using an optimized particle size distribution [13].

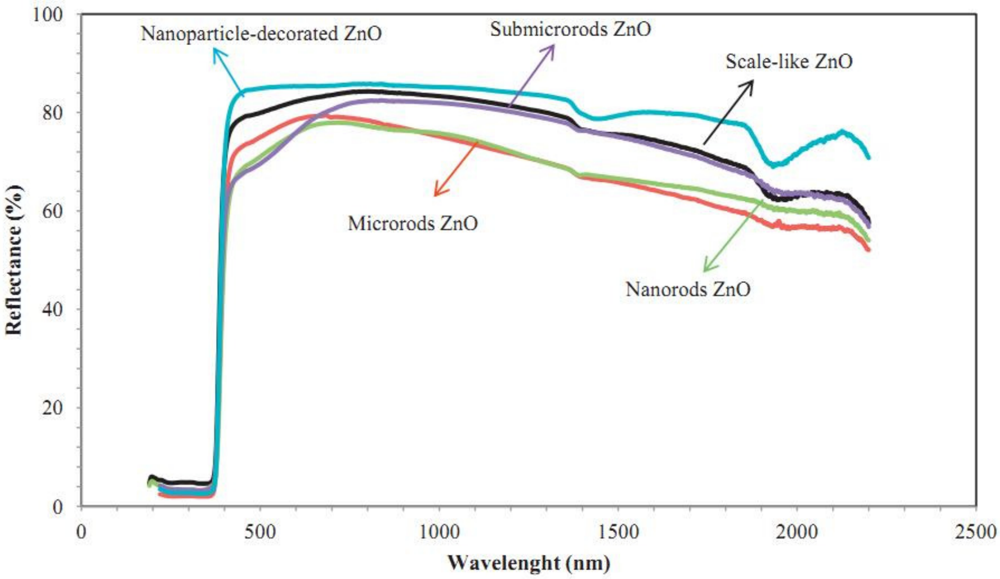

Figure 4 Experimental specular-included UV/VIS/NIR reflectance spectra of as-synthesized ZnO pigments [12].

Zinc oxide nanoparticles coated with zinc aluminate possess increased reflective performance compared with uncoated materials. In the region 400 - 800 nm, the coated nanoparticles possess 10 % more reflectance compared with uncoated nanoparticles [14].

Figure 4 shows the experimental specular-included UV/VIS/NIR reflectance spectra of as-synthesized ZnO pigments [12]. It can be seen that the pigment with optimized morphology would attain maximum diffuse solar reflectance. The results also indicated that the optical properties of ZnO powders were strongly affected by the particle size and morphology. A significant improvement in the scattering efficiency of ZnO pigment can be obtained using an optimized nanoparticle-decorated pigment.

5.2 OTHER TYPE OF METAL OXIDES AS NIR ADDITIVES

Cadmium stannate ($Cd_2•SnO_4$) is one of the most transparent, heat reflecting semiconductors. CdO, SnO_2 and CuCl are mixed thoroughly to make a homogeneous mixture and heated in an alumina crucible for six hours at 1050 °C. Cadmium stannate films on a silica plate reflect infrared light at approximately 1.5 microns film thickness. These films give 80 % reflectance at 2 microns film thickness and 90 % reflectance at 6 microns thickness. These properties make cadmium stannate films highly suitable for greenhouse window applications.

US Patent US6468647 describes the use of coloured metallic pigments such as aluminium and mica flakes for good infrared reflectivity [15]. According to the patent, colour has been incorporated on the metallic surfaces in such a way that it does not interfere with the ability of metallic pigments to control infrared reflectivity. Many commercially available pigments have been burnished into metallic surfaces to yield a modified surface, which retains the color of the pigment and gives very high infrared reflectivity.

Other materials having high refractive indexes are Fe_2O_3, Cr_2O_3, ZnS, Sb_2O_3 and ZrO_2. It is recommended that to achieve high reflectance over a wide spectral range, more than one type of material can be used.

6.0 EXPERIMENTAL

6.1 MATERIALS

Metal oxide nanostructures such as TiO_2 and ZnO were synthesized using an arc discharge apparatus developed in-house at GNS Science. A 99.9 % pure titanium/zinc rod served as the anode and a water-cooled 99.9 % pure Ti/Zn disc as the cathode inside the process chamber. The position of the anode was controlled by a stepper motor to facilitate an arc discharge with a steady current. During the experiment, air was introduced into the arc discharge chamber via a high precision leak valve once a vacuum level of 8×10^{-2} Torr was achieved. An arc was generated between the anode and cathode by a DC transferred arc process. Once the ambient operating pressure of air reached at 300 Torr, within a ± 5 Torr range of the target pressure, the arc was sustained with a constant power supply for the duration of each production run of 180 s. The arc current was kept at 60 to 120 A. A bulk quantity of materials with certain colour was observed adhering to the surface of the anode and the inner walls of the chamber.

6.2 ANALYSES METHODS

6.2.1 Morphology analyses

The collected powder was characterized using field emission scanning electron microscopy (SEM; JEOL 6500F) and high resolution transmission electron microscopy (HRTEM; JEOL 2100) to identify their morphology.

6.2.2 Reflectance measurement

When a beam of light falls on a powdered sample, reflection, transmission and absorption can occur. If the sample is optically thick enough, the transmitted light can be neglected. Reflection can be either specular reflection or diffuse reflection. Specular reflection is significant for optically smooth surfaces and for highly absorbing samples. Our powdered samples are not optically smooth, possess surface roughness and are nonabsorbing in the wavelength region of interest. Therefore, only diffuse reflection needs to be considered to the total reflected light for our samples.

The common method to examine the reflectance of a material is to measure its reflectance spectrum as a function of wavelength. A spectrophotometer system based around a GSA/McPherson 2051 metre focal length monochromator was used to measure the reflectance properties of the powders. Stray light filters together with a predisperser were fitted to the monochromator. A current regulated tungsten halogen lamp was used as the light source. The bandwidth was set to 1.6 nm for all the measurements. The spectrophotometer system was capable of measuring reflectance in the region of 700 - 2500 nm.

The reflectance was measured as relative reflectance, defined as the ratio of flux reflected by a specimen to the flux reflected by a reference surface. Pressed halon powder (PTFE powder) was used as the white reflectance reference. The sample port of the integrating sphere was tilted at an angle of 6° to the incident light so that specular reflectance was included in the measurement of reflectance. Corrections were made for the known reflectance of the halon reference and a black cone was used to correct for stray light. Up to

four test samples were mounted on a pneumatic driven sample changer along with the white reference and black cone. The monochromatic beam was focused to a spot approximately 4 mm x 4 mm on the sample. The detector used for NIR measurements was a Hamamatsu P4638 lead sulphide detector. The whole system was controlled using software written in LabVIEW.

7.0 RESULTS AND DISCUSSION

7.1 MORPHOLOGY

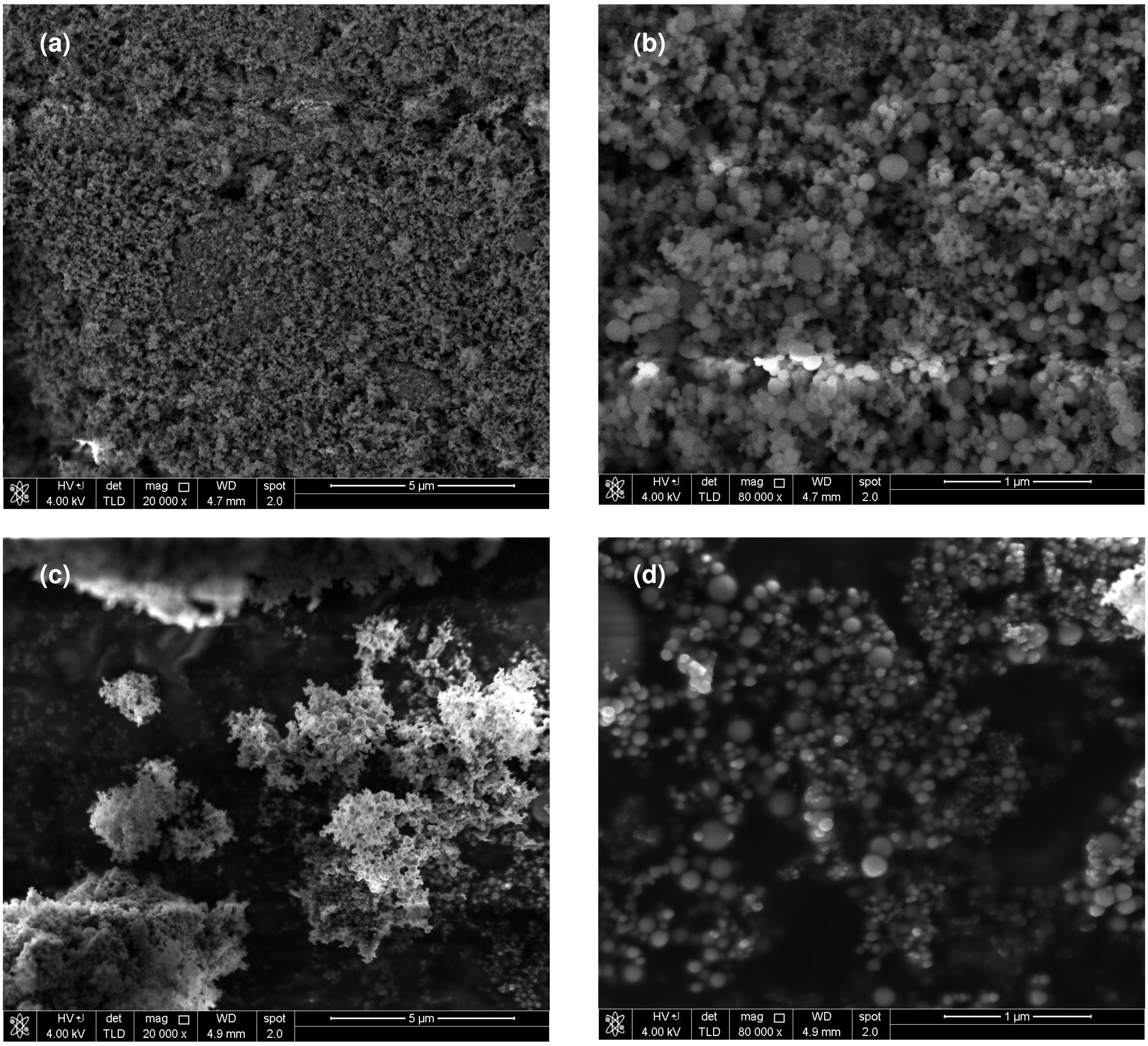

Figure 5 SEM images of TiO_2 nanoparticles synthesized by the arc discharge method at an arc current of 92 A ((a) low magnification and (b) high magnification) and 110 A ((c) low magnification and (d) high magnification), respectively.

Figure 5 shows the SEM images of as-synthesized TiO_2 structures by the arc discharge method. It demonstrates that the TiO_2 structures synthesized by the arc discharge method are predominately spherical particles. An arc current of 92 A was applied to obtain TiO_2 structures as shown in Figure 5(a) (low magnification) and 5(b) (high magnification). To study the effect of arc current on the material morphology, different arc currents (92 A and 110 A) were chosen in this work. Figure 5(c) (low magnification) and 5(d) (high magnification) show the TiO_2 obtained at an arc current of 110 A. It is evident that the arc discharge current has an effect on particle size. The TiO_2 particle size is in the range of 10 – 200 nm with a majority centred at 72 nm at an arc discharge current of 92 A (Figure 5(a) and 5(b)). After the arc current reaches up to 110 A, the obtained TiO_2 particle size has a majority centred at 85 nm and a few with size in the range of 100 nm to 220 nm (Figure 5(c) and 5(d)).

According to our previous results [16], the morphologies of the as-synthesized TiO_2 particles by arc discharge can be controlled by the arc discharge parameters, such as arc current – a higher arc discharge results in larger TiO_2 particle size.

7.2 NEAR INFRARED REFLECTANCE PROPERTIES

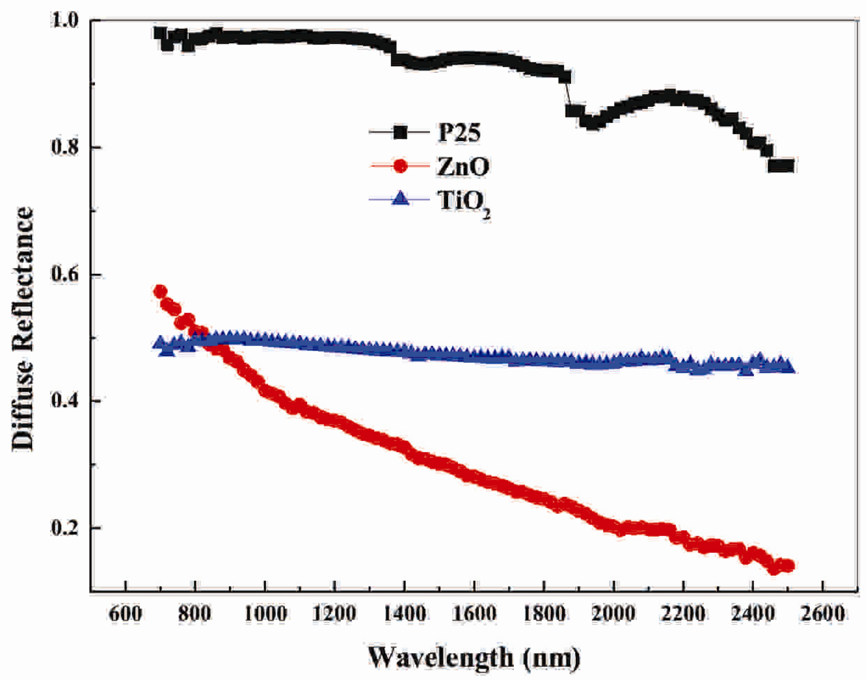

Figure 6 Near infrared reflectance spectra of P25 (commercially available TiO_2), ZnO and TiO_2 structures synthesized by arc discharge method.

Figure 6 shows the diffuse reflectance spectra of commercial TiO_2 powders (P25), TiO_2 and ZnO synthesized at GNS Science. In the powder reflection spectra, low reflectance values indicate high absorption in the corresponding wavelength region. As seen from the spectra, the diffuse reflectance for all three samples decreased with increasing wavelength in the range of 700 – 2500 nm. For commercial TiO_2, the diffuse reflectance decreased from 98 to 77 % in the NIR range (700-2500 nm). The reflectance for TiO_2 synthesized by arc discharge method decreased from 49 to 45 % while the reflectance for ZnO nanostructures decreased from 57 % to 14 %. Compared with P25 and ZnO, it is clear that the diffuse reflectance of TiO_2 doesn't change much in the wavelength of 700 – 2500 nm.

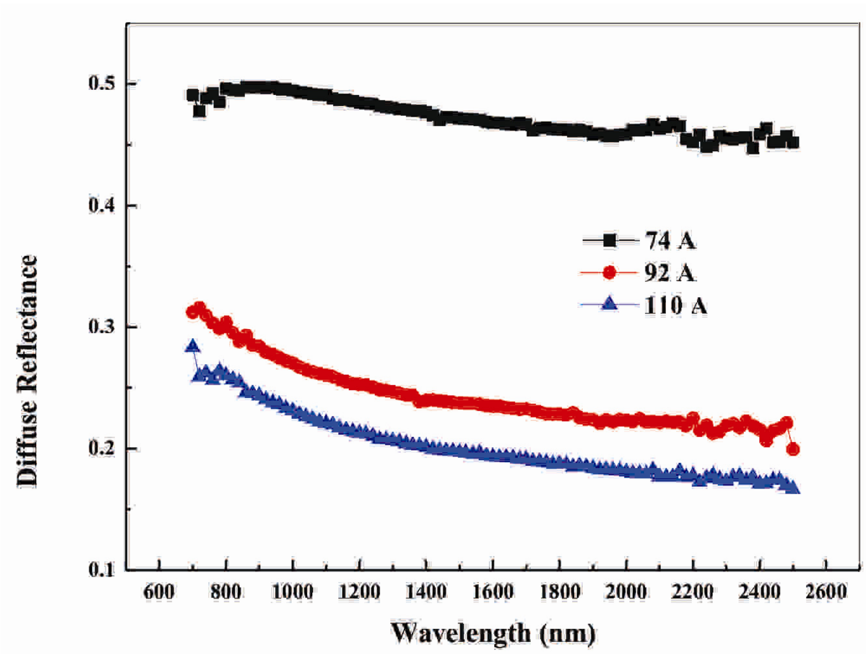

Figure 7 Near infrared reflectance spectra of TiO_2 powders synthesized by arc discharge method.

Figure 7 shows the diffuse reflectance spectra of TiO_2 powders synthesized at three different arc discharge currents (74 A, 92 A and 110 A, respectively). All samples show the same tendency in the measured reflectance data.

As seen from the spectra, The TiO_2 synthesized at:

- **74** A shows reflectance from **49** to **45** % in the NIR range (700-2500 nm).
- **92** A shows reflectance from **31** to **20** % in the NIR range (700-2500 nm).
- **110** A shows reflectance from **28** to **17** % in the NIR range (700-2500 nm).

It is clear that the TiO_2 synthesized at 74 A shows the highest reflectance in the NIR range compares with the other samples. Thus, it is concluded that with increasing arc discharge current, there is a decrease in the reflectance. According to the morphology study, TiO_2 powders synthesized at 74 A have the smallest particle size compared with other TiO_2 samples obtained at 92 A and 110 A. This can be explained by the relationship between the particle size and diffuse reflectance of particles.

Diffuse reflection occurs when the incident radiation penetrates into the sample powder and is reflected by grain boundaries of the particles. Diffuse reflectance depends on particle size and when the particle size decreases, the number of reflections at the boundaries increases. As a result, the depth of penetration of incident light decreases leading to a decrease in absorption. The net effect will be a decrease in the absorbed portion of light and an increase in the reflected portion of light. On increasing the particle size, the depth of penetration increases, as a result of less grain boundary reflections, and hence the reflectance decreases.

8.0 CONCLUSIONS

Heating of the exterior and interior of space is directly dependent on the absorption of electromagnetic radiation from the sun. The energy that is incident on the surfaces is approximately equally divided between UV/visible light (300 - 700 nm) and near infrared radiation (700 - 2500 nm). If the NIR portion of radiation could be reflected instead of absorbed by the surface, the exterior and interior temperatures could be significantly reduced. Therefore, a cool, non-white coating that absorbs in the visible range should be highly reflective in the near infrared part of the electromagnetic spectrum to maintain a high solar reflectance. The use of highly reflective “cool” coatings helps maintain lower exterior surface temperatures of roofs and building facades, and consequently contributes to increased indoor thermal comfort during the hot season, which reduces the need for cooling.

In general, the NIR reflectance of nanocrystalline oxides was 15 - 20 % higher than the macrocrystalines and minerals. Nanocrystalline metal oxides can be used as NIR reflective pigments in the region of 700 - 1300 nm. Potential applications of these pigments and products include refrigerated transport containers, roofs of the buildings and coatings in petroleum refineries to reduce evaporative losses of hydrocarbons.

We have successfully synthesized TiO_2 powders by an arc discharge method. Spherical TiO_2 nanostructures were obtained with an average diameter of 72 nm (range 10 – 200 nm) at an arc discharge current of 72 A. Diffuse reflectance was measured for the as-synthesized TiO_2 powders and it was found that TiO_2 nanostructures obtained at an arc current of 74 A had reflectance from 49 to 45 % in the NIR range (700-2500 nm). Also, we found that with increasing the arc discharge current, there was a decrease in the reflectance.

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