Modulating the Near Infrared Reflective Properties of Metal Oxides for Surface Coating Applications

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ABSTRACT

A colorant which is able to reflect the 49% of near infrared component of solar radiation is considered as a cool colorant. A two-fold approach to study the role of size and dopant on the near infrared reflective properties of metal oxide nanoparticles is reported in this work. It was found that the template assisted synthesis of α-Fe_2O_3, c-CoO, and sol-gel synthesis of Cr_2O_3 provided nanoparticles with very low size and uniform size distribution, which eventually translated into a high NIR reflectance. Cummative effect of size and doping was also found in the case of Cr_2O_3 nanoparticles doped with rare earth metal ions. This study conclusively provides an insight to how near infrared properties can be conferred to metal oxides with colors such as brown, black, blue and green through appropriate doping and size control.

Keywords: cool colorant, near infra-red reflectance, template synthesis, metal oxide nanoparticles, rare earth metal ion doping

1 INTRODUCTION

Inorganic solids acquire bright colors from electronic interband transitions in the visible region, intervalence charge transfer between transition metal ions and crystal field transitions. Owing to rising cost for cooling of building and automobiles, pigments which can serve as near infra-red (NIR) reflectors are sought. With 46% of the solar radiation being in the NIR region, it has been reported that the reflection of these radiations would considerably reduce heat build up. In recent years rare earth metal ion based pigments as cool colorants have been reported from our group. There are also reports which suggest that the NIR reflectance of pigments would also depend on factors such as particle size, size distribution, refractive index etc. Accordingly, this paper reports the independent and cumulative effect of size and doping on the NIR properties of metal oxide pigments.

2 MATERIALS AND METHODS

Iron oxide nanoparticles (α-Fe_2O_3) [1] and cobalt oxide nanoparticles (c-CoO) [2] were synthesized on a starch template as per procedure reported elsewhere. The Cr_2O_3 nanoparticles were synthesized by calcination from a chromium-urea complex.[3] The synthesized nanoparticles were characterized for its size and size distribution, crystallinity, crystal size and NIR reflectance.

3 RESULTS AND DISCUSSION

Powder XRD measurements of synthesized α-Fe_2O_3, c-CoO and Cr_2O_3 are presented in Figure 1. The XRD patterns have been indexed to the corresponding standards in the ICDD files. The crystallite size of the particles calculated using Debyee Scherrer Formula is reported in Table 1. Highly pure and crystalline products obtained in this work could be attributed to the high calcination temperature of about 800°C.

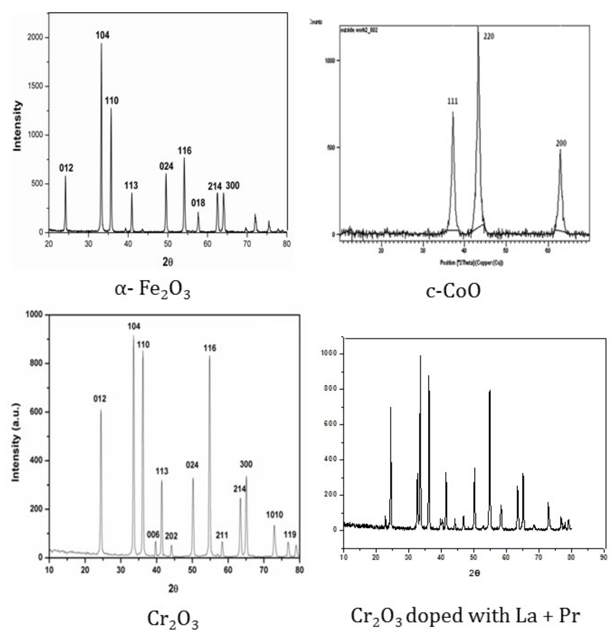

Figure. 1: XRD of synthesized metal oxide nanoparticles

The diffuse reflectance of the powdered pigment samples were measured (380–780 nm) with a UV–vis spectrometer (Lambda 35 with an integrating sphere attachment) using barium sulfate as reference. The measurement conditions were as follows: an illuminant D65, 10° complementary observer and measuring geometry d/8°. The CIE 1976 L*a*b* colorimetric method was used, as recommended by the Commission Internationale de l'Eclairage (CIE). In this method, L* is the lightness axis [black (0) to white (100)], a* is the green (+ve) to red (-ve), and b* is the blue (+ve) to yellow (-ve) axis. The CIELAB 1976 color coordinates for the synthesized nanoparticles are also presented in Table 1. Interestingly the lanthanum and praseodymium doping in Cr_2O_3 nanoparticles did not change the color coordinates significantly ($\Delta E = 12$).

System	Color	Color Coordinates			Crystal Size (nm)
		L	a*	b*	
α-Fe_2O_3	Brown	85	4.91	10.1	35±2
c-CoO	Black	75	0.11	7.70	27±3
Cr_2O_3	Green	42	-15.4	16.8	30±2
Cr_2O_3:La, Pr	Green	45	-10.9	6.7	34±1

Table 1: Crystal size, color and color Coordinates of synthesized oxides.

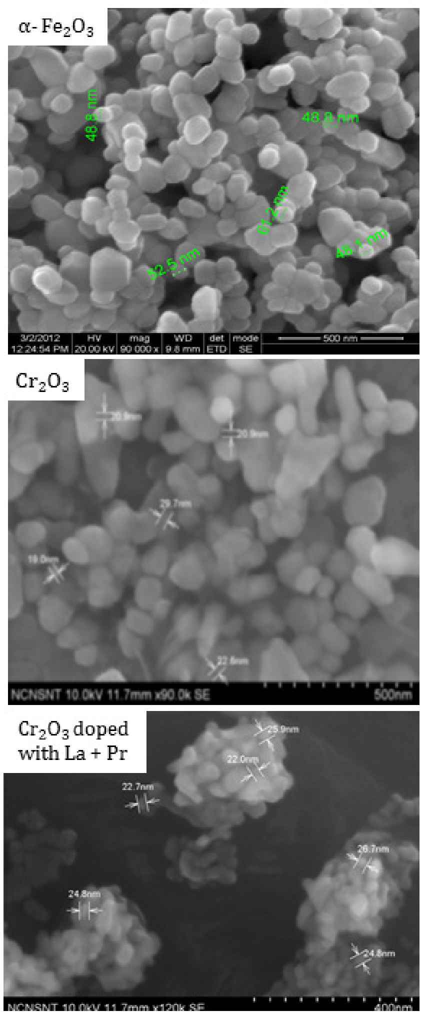

Figure 2: SEM image of nanoparticles

The particle size distribution in the case of nanoparticles was analyzed using photon correlation spectroscopy and found to be in the range of 25 – 50 nm. The corresponding SEM images are presented in Figure 2. It was observed that all the systems had good monodispersity, with average particle size of 48 nm for α-Fe_2O_3, and 25 – 35 nm for Cr_2O_3 and doped Cr_2O_3 respectively.

Roofs of buildings and automobiles that can reflect sunlight and keep the interiors cool in the sun, reducing demand for cooling power in conditioned systems and increasing occupant comfort in unconditioned systems is sought after in recent years. Visible light contains 52% power in the NIR region. A clean smooth white surface reflects both visible and NIR radiation, achieving a maximum solar reflectance of about 0.85. The NIR reflectance of the powdered pigment samples was measured with a UV–Vis–NIR spectrophotometer using poly-tetrafluoroethylene (PTFE) as a reference. Optical measurements were performed in the 700 to 2500 nm range. The reflectance spectra are presented in Figure 3. It can be found that pigments had a reflectance of 70 - 80% in the wavelength range of 1000 – 1500 nm.

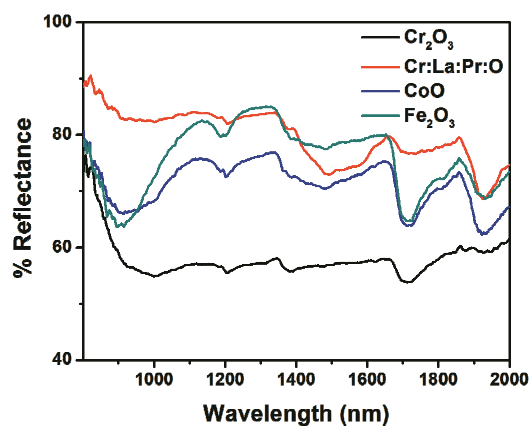

Figure 3: NIR spectra of the oxides

Brown and black colored pigments (α-Fe_2O_3 and c-CoO) are known absorbers of NIR radiation. However, in this instance their ability to reflect above75% NIR radiation is a result of size decrease, the depth of penetration of incident light decreases leading to 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. Reflectance is affected by a combination of mean particle size, size distribution, shape, porosity, packing density, surface texture and chemical composition.

In the case of Cr_2O_3 nanoparticles, the presence of rare earth elements is expected to enhance the NIR reflectance. While Cr_2O_3 nanoparticles had reflectance of 55% in the NIR region, the rare earth doped samples had a reflectance of 85%. Such an increasing trend is attributed to the presence of rare earth dopants.

The designed pigments displayed various color hues in the visible region but also possess high NIR solar reflectance and are excellent candidates for use as 'cool pigments'. Furthermore, the current pigments do not encompass any toxic metals ions and are hence considered as an environmentally benign class of inorganic pigments for various surface coating applications.

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