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Tailored properties of hematite particles with different size and shape

L. Demarchis*, F. Sordello, M. Minella, C. Minero

Department of Chemistry and NIS Center of Excellence, University of Turin, via Pietro Giuria 7, 10125, Turin (TO), Italy

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ABSTRACT

Red cubic and spherical hematite red cool pigments of different particle size were synthesized following two different methods. Cubic and spherical particles with larger particle sizes were obtained through a gel–sol method using chloride and nitrilotriacetate ions as shape controllers, and changing the starting temperature to control the final particles size. Smaller spherical particles were synthesized more rapidly following a catalytic phase transformation method in which the size control is obtained by varying the reagent concentration. Cool properties for the obtained particles were evaluated by calculating the solar reflectance for all hematite samples. The cool properties differ depending on the particle size and shape. By controlling the final size and morphology of pigment particles it is possible to obtain pigments with the desired cool properties. Pigment color properties were also evaluated using CIE XYZ and CIE xyY color spaces.

1. Introduction

The removal of natural vegetation and its replacement with buildings and paved surfaces [1] leads to an increase of temperature in urban city centers that in some cases can be also 10 °C higher than that of nearby rural places [2]. This phenomenon, termed the Urban Heat Island (UHI), has the effect of increasing the demand of energy (with a subsequent increase of energy supply costs), accelerating the formation of harmful smog and causing human thermal discomfort and health problems owing to the intensification of heat waves over cities [3,4].

Strategies for the mitigation of the UHI effects have been reported by Coutts et al. [5]. The development of new sustainable cities that use materials with high solar reflectance and thermal emissivity, the so-called “cool materials” has been proposed. Usually, cool materials are used to decrease the heat flow entering in a building. Their surface temperature is much lower than those of typical building materials and, if used on an urban scale, they help to decrease the air temperature of the urban environment reducing the harmful effects related to the UHI. Considerable interest has been directed to roofing materials [6–9]. Among these, white materials are obviously effective. Coatings with colored conventional pigments tend to absorb solar light (both Vis and NIR radiation, which conveys more than 50% of the sunlight power) resulting in heat accumulation [10]. The replacement of these conventional absorbing pigments with “cool pigments”, which absorb less NIR radiation, makes possible to produce coatings with higher solar reflectance, but similar in color to that of conventional or old-style roofing materials. Cool colored coatings can then be applied on roofs, building envelopes and other surfaces of the urban environment, such as exterior finishes and paints, or they can be used to produce building materials that reflect more sunlight than conventionally pigmented products.

For this purpose, in recent years pigments of different colors with cool properties have been commercialized. The color features of pigment materials (one or more) depend on their visible absorption, on their size (which varies scattering properties), and on their composition [11]. To tune the color properties of a material, pigments with different chemical compositions are used. Sometimes, cool pigments contain environmental unfriendly metals such as Group V and rare earths [12], or are toxic, containing Cd or Cr. The main proposed cool pigments contain inorganic complex, such as chromium green, cobalt blue, cadmium stannate, lead chromate, cadmium yellow and chromium titanate [10,13]. Among NIR reflective pigments with promising characteristics there are rare earth mixed oxides such as Me_xMnO_y (where Me = Y, Ce, Pr, Nd and Sm [12,14]), or rare earth metals – molybdenum mixed oxides such as Y_6MoO_{12} [15]. Another approach is the use of pigments with particles coated with a metallic film [16]. The main drawbacks of the cool pigments obtained with the aforementioned approaches are their high costs.

* Corresponding author. Tel.: +39 0116705298.
E-mail address: luca.demarchis@unito.it (L. Demarchis).

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The choice of color depends on tradition and aesthetic needs, e.g. Italian traditional roofs are dark red, while in Thailand they are green. A database with optical characteristics of a huge number of pigments [17] is available to assist the optimization of the solar reflectance for industries which operate in the building sector. In the cited database there are four red pigments based on iron oxides.

In this work, we report the synthesis and investigation of red hematite-based cool pigments. It is known that for a given material (and for given optical constants) the optical properties depend on size, morphology and cluster aggregation of particles, so a set of syntheses was performed to obtain hematite particles with different size and shape. The optical properties of all the synthesized samples were analyzed with the aim to give insight into the relation between these properties and the morphological features of the pigment particles. We obtained different kinds of morphology suitable for cool pigment applications.

2. Materials and methods

2.1. Materials

The hematite particles were synthesized using iron (III) chloride hexahydrate (Sigma–Aldrich, >99%), iron (II) chloride tetrahydrate (Fluka, >99%), sodium hydroxide (Sigma–Aldrich, >99%), hydrochloric acid (Carlo Erba, 37%), nitrilotriacetic acid trisodium salt (Fluka, >98%), sodium sulphate (Aldrich, >99%) and sodium chloride (Carlo Erba, >99.5%). For sample washing, 1 M ammonia solution (Fluka, 25%) and 0.5 M sodium nitrate solution (Sigma–Aldrich, >99%) were utilized. Ultra-pure water produced by a Milli-Q™ system (Millipore) was used. Commercial polyacetovinyl emulsion (Vinavil NPC, Vinavil SPA) was used as dispersing medium for the preparation of paints.

2.2. Hematite syntheses

In literature several synthetic methods to produce hematite particles are reported [18,19]. In this work, monodisperse hematite particles with different size and shape have been obtained following two different procedures.

i) The first method was a gel–sol transformation procedure proposed by Sugimoto [20]. The standard condition for the syntheses were as follow: NaOH (6 M, 45 mL) were slowly added to magnetically stirred $FeCl_3$ (2 M, 50 mL) solution. Chloride or nitrilotriacetate (2.5 M, 2 mL) were then added to the $Fe(OH)_3$ gel to obtain pseudocubic or spherical particles, respectively. The slurry was then kept under stirring for additional 10 min. The obtained $Fe(OH)_3$ gel was then transferred into a tightly stoppered Pyrex bottle (Schott Duran) and heated at 100 °C for at least 3 days until the conversion occurred (HAZARD – heating sealed reaction vessels must only be undertaken using appropriately designed equipment with pressure relief valves under rigorously controlled conditions behind a suitable protective shield). Hematite samples with different particle size were synthesized varying the pH and the temperature of the $FeCl_3$ solution when NaOH was added.

ii) The second method follows the catalytic phase transformation mechanism proposed by Liu and co-workers [21]. Standard syntheses were performed as follow: NaOH (6 M) was slowly added to 50 mL of a magnetically stirred $FeCl_3$ solution (2 M, unless for experiments in which [Fe(III)] was changed) until pH 7 (typically ca. 49 mL). Then, $FeCl_2$ (ca. 0.40 g) was added in the ratio [Fe(II)]/[Fe(III)] = 0.02 to the gel and pH was readjusted to 7 adding dilute NaOH. The slurry was kept under stirring for additional 10 min and then refluxed (for at least 30 min) until conversion to hematite occurred. The concentration of $FeCl_3$, the amount of Fe(II), the pH and the temperature were varied to obtain samples with different particle size.

After heat treatment, all the as-prepared hematite samples were washed with ultra pure water three times, once with 1 M NH_3 and three times again with ultra pure water. The pigments were separated from the supernatant with centrifugation at 1370 × *g* (3500 rpm for 30 min, using an ALC PK131R Multispeed Refrigerated Centrifuge). Then each sample was dried at 70 °C.

2.3. Hematite characterization

The crystalline phase of the samples was identified with X-ray Diffraction and Raman analyses. X-ray powder diffraction (XRD) patterns have been recorded with a PW3050/60 X'Pert PRO MPD diffractometer from PANalytical working in Bragg–Brentano configuration. The X-ray source was a high power ceramic tube PW3373/10 LFF with a Cu anode and the instrument was equipped with a Ni filter to attenuate Kb. Diffracted photons were collected with a real time multiple strip X'celerator detector. Powder samples have been hosted on SiO_2 amorphous sample holder. Raman spectroscopy analyses were performed with a LABRAM HRVIS (Jobin Yvon), fitted with an Olympus BX41 optical microscope. Raman spectra were excited using the 533 nm line of a Nd solid state laser. The laser power was 100 mW. Spectra were collected over the range 80–1525 cm^{-1} at a resolution of approximately 2 cm^{-1}.

Size and shape of synthesized hematite particles were determined through scanning electron microscopy by a Scanning Electron Microscope Zeiss model EVO-50 XVP operating at 15 kV, beam current 50.0 μA, probe intensity 50 pA.

The particle hydrodynamic radii were determined by photon correlation spectroscopy, also known as Dynamic Light Scattering (DLS). The used instrument was an ALV-NIBS High Performance Particle Sizer (ALV GmbH, Germany) equipped with a Ne–He laser and with an ALV-500 multiple tau digital correlator. Samples were suspended in ultra-pure water, and analyzed by recording the intensity of the scattered light at an angle of 173° for 30 s at 25 °C. Suspensions with different hematite loadings were analyzed, and the results were extrapolated at infinite dilution.

2.4. Optical properties evaluation

Total reflectance analyses were carried out to determine scattering properties of the samples using a dual-beam Varian Cary 5000 UV–VIS–NIR Spectrophotometer with an integrating sphere. The internal walls of the sphere are coated with poly(tetrafluoroethylene) (PTFE) and $BaSO_4$ was used as reference material. Light sources are a deuterium lamp in the 185–350 nm range and a halogen lamp in the 350–3300 nm range. The detection is performed by means of R928 PMT (185–800 nm) and Cooled PbS (800–3300 nm) detectors. The analyses were performed over the range 200–2500 nm. To estimate the solar reflectance (*SR*) of obtained hematite, the total reflectance data were weighted on solar irradiance data for each sample following the equation:

$$SR = \frac{\int_{280}^{2500} P_{solar}(\lambda) \cdot R(\lambda)}{\int_{280}^{2500} P_{solar}(\lambda)} \quad (1)$$

in which $P_{solar}(\lambda)$ is the Air Mass 1.5 solar irradiance (ASTM G-173-03 Reference Spectra, Global Tilt data) [22]; $R(\lambda)$ is the measured