

Acrylic acid in the synthesis of a trimetallic nano oxide as NIR reflectance pigment via polymer pyrolysis method

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ABSTRACT

Recently, the polymer pyrolysis method by means of acrylic acid and metal salts has been developed for preparation of different metal oxides. The co-polymeric precursor compounds are schematically supposed to have metal ions attached by the ionic bonds to carboxylate ions in a polymeric chain or between the polymeric chains. This uniform distribution of metal ions and $\text{Ti}(\text{OH})_4$ in the precursor favors the formation of uniformly distributed solid solution of the metallic oxides in the pyrolysis process. In this work, a trimetallic oxide as a pigment with high near-infrared (NIR) reflectance was synthesized by reaction of titanium butoxide with metal acetate ($\text{M} = \text{Mn}, \text{Ni}, \text{Ti}$) in acrylic acid via polymer pyrolysis method. The pigment properties of the oxide were investigated by X-ray diffraction (XRD) and field scanning electron microscopy (SEM), NIR diffuse reflectance spectroscopy (DRS).

Keyword

Acrylic acid, Polymer pyrolysis, Metal oxide, NIR reflectance

1. Introduction

Large-scale application of metal oxides with nanometer size as cool colors with special optical properties have prompted the development of several widely used methods, including sol-gel coprecipitation, milling, hydrothermal method [1-10]. The above methods can produce highly crystalline and uniformly sized nanoparticles. However, these approaches suffer from some limitations since they usually require a large quantity of solution and organic materials, long processing time, heat treatment for crystallization, filtration, and dry process. Thus, it is of practical importance to seek for a novel method for preparation of metal oxide nanoparticles [11]. The polymer pyrolysis method has some advantages in preparation of nanoparticles: (a) easy operation, (b) easy scale-up in batch form and (c) production of highly homogeneous nanocrystalline particles with excellent magnetic, electrical and optical properties. In addition, this method is versatile for various metals and thus should also be suitable for preparation of inorganic nano-pigments [3]. This method is versatile so that various metals can be used. It involves the preparation of a polymer precursor that reflects the precise stoichiometry of the end product and allows preparation nanoparticles with a narrow size distribution at a moderate temperature [12]. First, the Ni-Ti precursor was made via in situ polymerization method. Subsequently, green $\text{Mn}_x\text{NiTiO}_{3+x}$ nanoparticles were prepared by pyrolyzing the polymer precursor at a moderate temperature. Finally, the structural properties and optical properties are discussed.

2. Experimental

The chemical reagents tetra-n-butyl titanate ($\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$), nickel (II) acetate ($\text{Ni}(\text{CH}_3\text{COO})_2$), manganese (II) acetate ($\text{Mn}(\text{CH}_3\text{COO})_2$), ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$), and acrylic acid (CH_3COOH) are used without any further purification processes. In a typical experiment, $\text{Ni}(\text{CH}_3\text{COO})_3$ (0.003 mol),

Mn(CH₃COO)₃ (0.001 mol) and Ti(C₄H₉O)₄ (0.003 mol) were added into 20 g of CH₃COOH aqueous solution (CH₃COOH·H₂O = 70:30 wt %) under magnetic stirring. Afterward, a small amount (1 g) of 5 wt % (NH₄)₂S₂O₈ aqueous solution as initiator was added to the mixed CH₃COOH solution to promote the polymerization. Under heating at 90 °C, the mixed solution was stirred for 20 min to form the well distributed polyacrylate precursor. The obtained precursor was dried and then, calcined at 600 °C to obtain Mn_{0.33}NiTiO_{3.33} green pigment.

3. RESULTS AND DISCUSSION

Nanopigments were prepared by a polymer pyrolysis method. The polymeric precursors were made by in situ polymerization of the mixed aqueous solution of acrylic acid in the presence of metal salt with (NH₄)₂S₂O₈ as the initiator. This affords a composition which has the predetermined ratio of Ni to Mn to Ti (3:1:3) to be compatible with the final product according to the following reactive formula.



With the existence of a large amount of H₂O, Ti(C₄H₉O)₄ mainly hydrolyze with the water in situ and lead to an immediate nucleation of Ti(OH)₄, which is distributed randomly within the polymer precursor, as shown in Figure 1 [4].

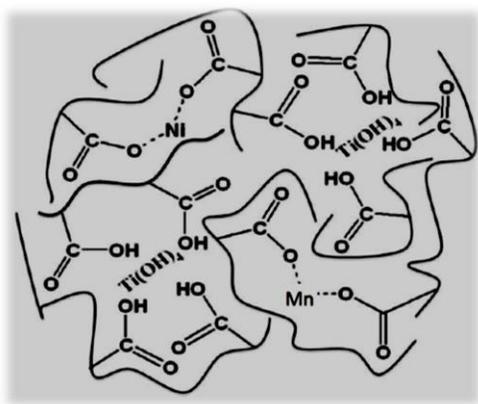


Fig.1. Schematic representation of polymeric chain for the co-polymeric precursor of Mn-Ni polyacrylates.

The Ni (II) and Mn (II) ions are bound by the strong ionic bonds between the polymeric chains. Ti(OH)₄ is distributed randomly within the polymer precursor. This uniform immobilization of metallic ions in the polymer chains favors the formation of NiTiO₃ nanoparticles in the following pyrolysis process. In addition, this method can be versatile to easily synthesize other complex inorganic colored pigments [3].

Fig. 2 shows XRD pattern of sample calcined in 600 °C for 2 hours in air. Particle sizes were calculated by Scherrer equation had a value of 94.2 nm.

$$D_{hkl} = \frac{K\lambda}{\beta_{hkl} \cos \theta}$$

2 Theta (degree)	Theta (degree)	Theta (rad)	FWHM (rad)	k	lambda	Nanocrystal size
37.584	18.6	0.3236	0.001473	0.9	0.15406	94.2

The diffuse reflectance of the samples in the NIR region has been investigated (Fig. 3). It can be seen that the reflectance is average 50% thus this pigment can be used as a cool color.

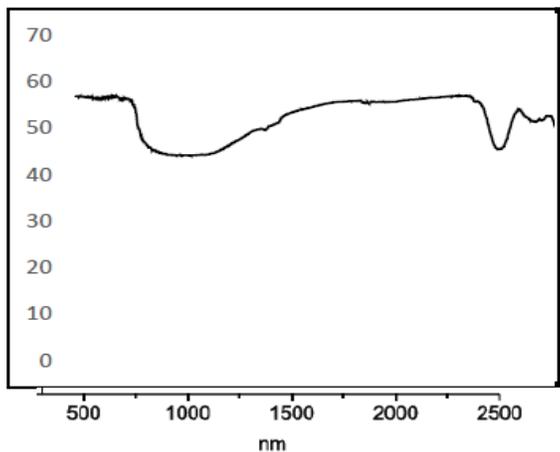


Fig. 3. The reflectance spectra of sample

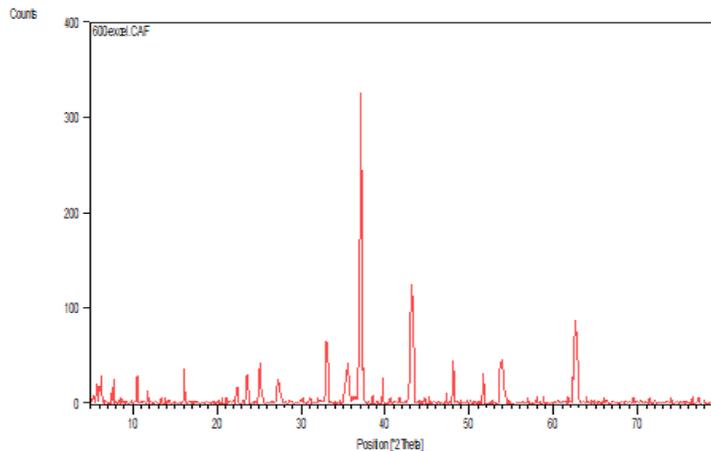


Fig. 2. XRD pattern of pigment powder sample

As shown in Fig. 4, the morphology and particle sizes of the prepared nanoparticles are confirmed by SEM images.

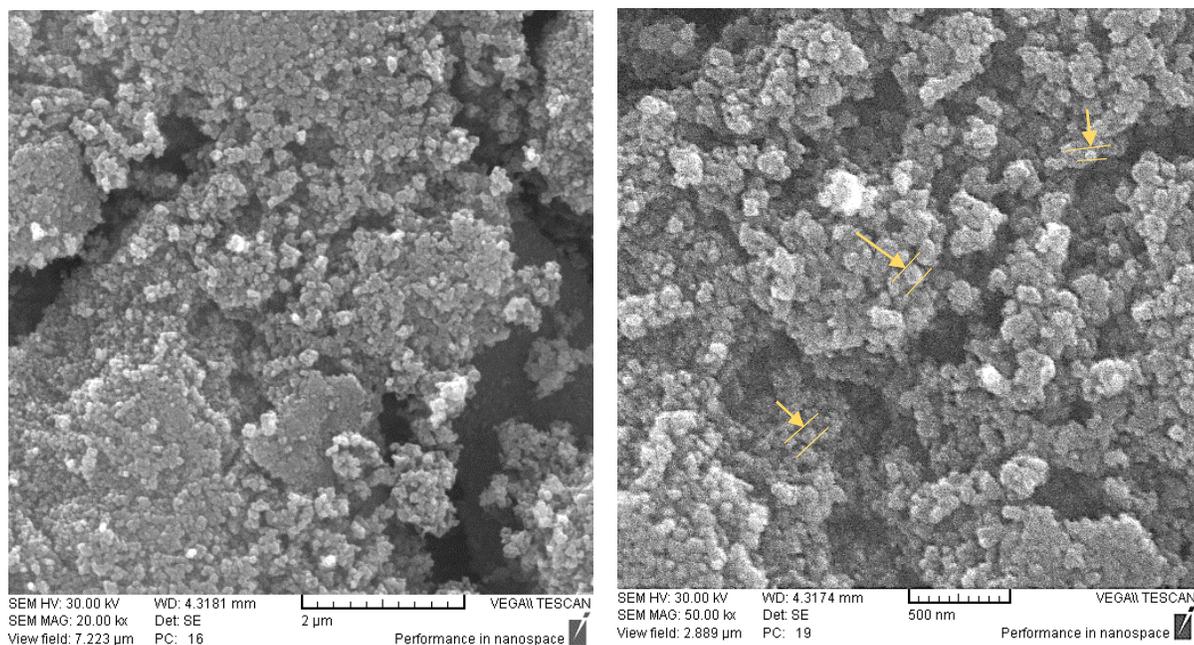


Fig. 4. SEM images of pigment nanoparticles with average of 100 nm

4. Conclusion

This report describes a novel route of producing highly homogeneous nanoparticles by the pyrolysis of a Mn-Ni-Ti copolymeric precursor in situ polymerized by reaction of the metal salts and acrylic acid as a polymeric template. Copolymeric precursor were calcined at 600°C. Prepared pigment were synthesized in nano scale of 94 nm which were confirmed by XRD pattern and SEM images. The reflectance spectra show that the sample has given an average NIR solar reflectance of 50% which makes this green pigment suitable as a cool color.

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