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Characterization and synthesis of nanometer magnetite black pigment from titanium slag by microwave-assisted reduction method

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ABSTRACT

The comprehensive utilization of titanium slag can not only reduce pollution, but also bring considerable social and environmental benefits. Nanometer magnetite black pigment has been synthesized by microwave-assisted reduction method under nitrogen. The properties of nanometer magnetite black pigment were investigated by X-ray diffraction, Fourier transform infrared spectroscopy, Raman spectroscopy, field emission scanning electron microscopy, energy dispersive spectrometry, transmission electron microscopy, selected area electron diffraction, X-ray photoelectron spectroscopy, thermal gravimetric-differential scanning calorimetry, zeta potential, Brunauer–Emmett–Teller method and colorimetric analysis. The formation of nanometer magnetite black pigment was confirmed by XRD, FTIR, RM and XPS. FESEM and TEM indicated that nanometer magnetite pigment with the average diameter of ~52 nm was virtually spherical, having a porous structure. The BET surface area and the pore volume of nanometer magnetite black pigment were found to be about 18.48 $m^2\ g^{-1}$ and 0.081 $cm^3\ g^{-1}$ respectively. The TG-DSC analysis shows that nanometer magnetite black pigment has good thermal stability in low temperature. Nanometer magnetite has good dispersion by zeta potential analysis in water. Besides, nanometer magnetite black pigment exhibits a promising prospect of application in water-based pigment.

1. Introduction

Titanium slag is an industrial solid waste from the production of titanium dioxide by digesting ilmenite ($FeTiO_3$) with sulfuric acid [1], and the major composition of titanium slag is ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$). In China, 98% of titanium dioxide was manufactured by digestion with sulfuric acid, and this process generated a large amount of titanium slag [2,3]. It has been reported that the total production of titanium slag was more than 3 million tons in 2016, and the annual growth rate of solid waste exceeded 10% in China [4,5]. However, only a few part of titanium slag was reused and the rest was still disposed of as industrial solid waste. Enormous quantities of titanium slag not only resulted in severe environmental pollution, but also caused great waste of iron resource. In consequence, there is an urgent need to utilize titanium slag in an effective way.

Nanometer-sized magnetite ($FeFe_2O_4$) black pigment has been widely applied in many fields, such as construction materials, paints, coatings, cosmetics and paper due to the fact that it has nontoxicity, stable color tone, excellent dispersion, high tinting strength and hiding power [6]. In this context, the key of the problem is how to use titanium slag for synthesizing nanometer-sized magnetite pigment. Presently, synthesis methods of nanometer-sized magnetite pigment such as chemical co-precipitation [7], thermal decomposition method [8], micro-emulsion method [9], and hydrothermal method [10], have been reported. However, the above-mentioned methods were limited due to their complex synthetic process and high costs. Herein, it is very necessary that an economical and simple method to synthesize nanometer-sized magnetite pigment is developed.

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Microwave-assisted reduction method was one of the most effective synthetic methods to synthesize nanometer-sized magnetite pigment due to simple technological route and easy operation. Moreover, microwave-assisted synthesis had the advantages of high reaction rates, short reaction time, efficient energy transformation and uniform heat distribution [11]. What is more, microwave assisted reduction method is suitable for mass production and meets the cleaning production requirements and generates better benefits on economy, society and environment. Hence, microwave-assisted reduction method might be a promising method for synthesizing nanometer-sized magnetite pigment.

The aim of this paper is to synthesize nanometer magnetite pigment from titanium slag as a starting material by microwave-assisted reduction method under nitrogen. The properties of nanometer magnetite pigment were analyzed by X-ray diffraction, Fourier transform infrared spectroscopy, Raman spectrum, field emission scanning electron microscopy, energy dispersive X-ray spectrometry, transmission electron microscopy, thermal gravimetric-differential scanning calorimetry, X-ray photoelectron spectroscopy, zeta potential, Brunauer–Emmett–Teller method and colorimetric analysis.

2. Experimental

2.1. Materials

Titanium slag used in this study is from Titanium Company of Pangang Group Corp (Sichuan, China), and its chemical composition is given in Table 1. Pyrite, an industrial solid waste from mineral processing plants, is derived from Hanyuan Chemical factory (Sichuan, China), and the main chemical composition is listed in Table 2. Titanium slag and pyrite were used as receive without additional purification. Water used in the experiment was deionized (DI) water with a resistivity of 18.2 MΩ cm.

2.2. Preparation of nanometer magnetite pigment

Nanometer-sized magnetite pigment was synthesized from titanium slag (waste ferrous sulfate) by microwave-assisted reduction method under nitrogen protection according to the following equation:

$$1FeSO_4 + FeS_2 \rightarrow 6Fe_2O_3 + 13SO_2(g) \quad (1)$$

$$16FeSO_4 + FeS_2 \rightarrow 11Fe_3O_4 + 2SO_2(g) \quad (2)$$

Briefly, titanium slag and pyrite were separately dried at 105 °C for 420 min, and then the mass ratio of pyrite to titanium slag was adjusted to 1:6. The resulting mixture was heated to 500 °C at the heating rate of 40 °C·min^{-1} in a microwave oven (Model HY-ZC1512, 2450 MHz, China) under N_2 (15 ml min^{-1}). The output power was controlled at 800–1000 W during microwave heating. The sample was kept at 500 °C for 1 min before being cooled to room temperature. Finally, the obtained sample was washed repeatedly with ethanol and DI water to remove impurities, and dried under vacuum at 80 °C for 360 min. In addition, sulfur dioxide produced during reaction process was absorbed directly with water to prepare sulfuric acid.

Table 1
The chemical composition (wt. %) of the titanium slag.

Component	Fe_2O_3	SO_2	MgO	TiO_2	MnO_2	V_2O_5	CaO	Al_2O_3	SiO_2
wt. %	53.96	43.44	2.10	0.24	0.11	0.02	0.01	0.01	0.01

Table 2
The chemical composition (wt. %) of the pyrite.

Element	Fe	S	Zn	Ca	Mg	Si	Pb	Cu	C	O
wt. %	35.29	41.02	1.39	3.55	2.13	1.21	0.88	0.04	2.13	12.22

2.3. Characterizations

The X-ray powder diffraction (XRD) analysis of the sample was performed using an X'Pert PRO diffractometer (Empyrean, PANalytical) with CuKα radiation (λ = 1.5408 Å). Surface functional groups of the sample were identified by Fourier transform infrared spectroscopy (FTIR, Nicolet 6700, USA). Raman spectroscopy (RM) was done on a dispersive micro-Raman spectrometer (LabRAM HR, Horiba) equipped with a 532 nm laser. Surface morphology of the sample was studied by field-emission scanning electron microscope (FESEM, FEI Quanta-250), coupled with an energy dispersive X-ray spectrometry (EDX), and transmission electron microscope (TEM, FEI Tecnai-G2). Oxidation state of the sample was analyzed by X-ray photoelectron spectroscopy (XPS) using XSAM800 analyzer. Nitrogen adsorption-desorption isotherm was recorded using a surface area analyzer (ASAP2020, Micromeritics Instrument Corp.) based on Brunauer-Emmett-Teller method. Thermogravimetric-differential scanning calorimetry (TG-DSC) was performed on a synchronous thermal analyzer (STA449 F3, NETZSCH, Germany) under nitrogen flow (20 ml min^{-1}) at the temperature range of 35–900 °C at a heating rate of 20 °C·min^{-1}. Zeta potential (ζ) under different pH values was determined with a Malvern brand analyzer (Zetasizer Nano, ZS90, UK). The CIE-L*a*b* chromatic coordinates of the sample were recorded on a spectrophotometer (X-Rite, Ci7800), employing D65 illuminant and barium sulfate was used as a white reference.

3. Results and discussion

3.1. X-ray diffraction pattern

The X-ray powder diffraction pattern for nanometer magnetite pigment is illustrated in Fig. 1. As can be seen from Fig. 1, the characteristic peaks of nanometer-sized magnetite pigment is consistent with the standard diffraction patterns of magnetite (ICDD PDF 19–0629) with inverse spinel crystal structure, without any other phase diffraction peak, demonstrating the formation of nanometer-sized magnetite pigment. Besides, the diffraction peaks observed at $2\theta = 18.34°, 30.20°, 35.53°, 37.17°, 43.18°, 53.50°, 57.05°$ and 62.67° are corresponded to lattice planes of (111), (220), (311), (222), (400), (422), (511) and (440) respectively. The crystallite size

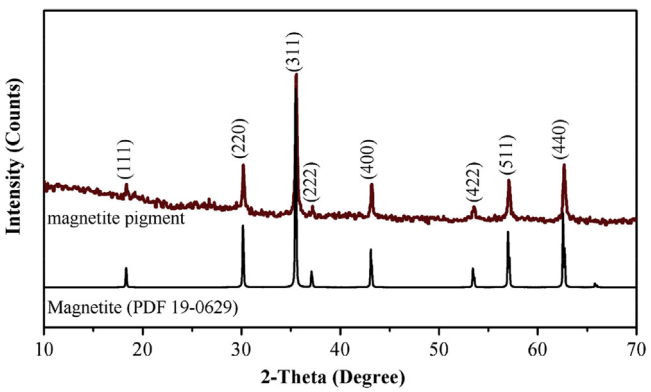

Fig. 1. X-ray powder diffraction patterns of nanometer-sized magnetite pigment.