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Cleaner production of spherical nanostructure chromium oxide (Cr_2O_3) via a facile combination membrane and hydrothermal approach

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ABSTRACT

Chromium oxide is widely used in national defense, hard alloy, alloy, pigment, vacuum plating, consumables and high purity alloy and belong to one of the main products of chromate production industry. In the present study, a novel cleaner process is proposed to synthesize nanostructure chromium oxide (Cr_2O_3) from waste source containing chromium (VI). Hydrated chromic oxide was prepared by combination membrane and hydrothermal method. After calcined, chromium (III) compound: nanostructure chromium oxide (SNCO) was obtained. In the membrane electrolyte stage, this way can reduce the amount of acid added to adjust the solution pH. Besides, addition of CO_2 into the cathode compartment could improve the current efficiency and desalination efficiency, while decrease the energy consumption. Then the products were characterized. Combined with the experiment results of TGA and XRD, the potential formation mechanism of hydrated chromic oxide was proposed. The fine structure of the product was analyzed by SEM and TEM. It was proved that the nanostructure chromium oxide with good crystallinity was obtained. The UV–Vis was used for optical properties, which proved that it had good optical properties.

1. Introduction

Chromium and its compounds have wide industrial applications, such as, metallurgy, leather, semiconductor, pigments, dyes, spices, metal surface treatment, wood preservation, military, hydrogen sorption materials and other industries, which was listed as one of the most competitive products of eight kinds of resources (Bijker et al., 2003; Bobet et al., 2003; Wang et al., 2007). For most chromium compounds, chromate and chromium oxide are the starting material, either directly or indirectly through intermediate steps. The traditional chromate production process used in China presently consists of three procedures: roasting of chromite ore, water leaching, and multi-stage evaporation and crystallization. The utilization of reagents and energy in the calcination process is generally quite low (Xu et al., 2006). Furthermore, chromate plants discharge large amounts of chromium-containing residues, dusts and waste gases, creating serious pollution problems that threaten underground waters, rivers, marine areas, and human health (Kowalski and Mazanek, 1998; Walawska and Kowalski, 2001). All of these processes have pollution problems from chromium (VI) residue. Therefore, extensive research has been carried out on the utilization and treatment of chromium ore processing residues (Liu et al., 2014).

In the case of Hinkley (a small desert town in San Bernardino Country, USA) chromium (VI) was used by Pacific Gas and Electric Company (PG&E) in cooling systems to prevent pipes from rusting. The runoff of chromium (VI) wastewater on the PG&E property, seeped into the ground and contaminated local water supplies. PG&E was required to compensate the plaintiffs $333 million for the chromium (VI) contamination. This is the highest compensation award in metal toxicity history. A similar case occurred in 2007 in the Asopos River, near Oinofyta, Greece. In June 2009, the ground water in Midland, Texas (USA) was found to be contaminated with chromium (Saha and Orvig, 2010). The occurrences of hexavalent chromium are growing, particularly with state-wide hexavalent

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chromium sampling with lower detection limits mandated for water supplies by the California Department of Health Services (DHS) because of increasing health concerns (Saha et al., 2011). Chromium is a primary contaminant at over half of all superfund hazardous waste sites. At present, the common method to deal with the chromium (VI) pollution is to reduce Cr (VI) to Cr (III) by various chemical reagents. One of the main products is chromium oxide (Cr_2O_3).

Chromium oxide is an important environmental-friendly chemical with numerous industrial applications. It could be served as pigments in paints and coatings, enamels, additives in concrete and other building products, floor coverings (Xu et al., 2006). Therefore, an important topic in the chromate industry is how to realize cleaner production of chromium compounds without producing chromium-containing residues, and many techniques have been studied. Study on chromium oxide has become a hot area. In the current, various preparation methods for chromium oxide have been proposed, such as, mechanochemical processing (Tsuzuki and Mccormick, 2000), combustion method (Lima et al., 2006), hydrothermal reduction method (Pei et al., 2009), sol-gel (El-Sheikh et al., 2009; Kawabata et al., 1995), chemical vapor deposition (Chevalier et al., 2000), hydrolytic co-precipitation method (Zhang et al., 2014) and using EDTA as a chelating agent to synthesize Cr_2O_3 nanopowders (Aghaie-Khafri and Kakaei Lafdani, 2012). Among all synthetic methods, the hydrothermal synthetic method has showed an extraordinary ability in the controllable fabrication of inorganic nanostructures (Byrappa and Adschiri, 2007; Rajamathi and Seshadri, 2002; Yao and Yu, 2007). Wei et al. (Wei et al., 2015) have prepared chromium oxide green pigment by thermal decomposition of chromium hydroxide via hydrothermal reduction of a high concentration mixture of Na_2CrO_4 using $NaHCO_3$ and urea as mineralizers. And investigated the effects of mineralizers on the hyrothermal reaction process, conversion of chromate, properties of morphous $Cr(OH)_3$, and color performance of Cr_2O_3. Pei et al. (Pei and Zhang, 2013) have obtained large Cr_2O_3 polyhedrons with the sizes of 9–18 μm under the assistance of citric acid in hydrothermal system.

However, there is little attention to control the pH by membrane method in the preparation process of chromium oxide. Membrane technology has obtained wide application in industry and research centers for recent years (Gohil et al., 2006). Good selectivity, stability, and nonfouling, these properties have made ion exchange membrane become an important method in chemical and waste treatment applications, such as desalination of brackish water, recovery of valuable metals from effluents industry (Hosseini et al., 2010; Li et al., 2005; Xu, 2005), in food and pharmaceutical industry. High permselectivity, low electrical resistance, and high chemical, mechanical and thermal stability are always the purpose for ion-exchange membranes in electro-dialysis application (Tuan et al., 2008). Electro-dialysis is a separation process that ions are transported through membranes by the application of a consequence of a direct electric current and as an electrical potential difference (Gohil et al., 2004; Shahi et al., 2002).

In the present work, in order to avoid the problem of existing chromium (VI) pollution, a novel environmental-friendly approach: combination membrane and hydrothermal method was proposed to synthesize chromium oxide from chromium (VI) waste resource. This work was intended to determine an environmental-friendly approach to utilize chromium waste resource and solve the pollution problem of hexavalent chromium. Therefore, cleaner production of chromium could be realized. Thermogravimetric analysis (TGA) and X-ray diffraction (XRD) were used to determine the thermal decomposition of hydrated chromic oxide and the crystal structure of chromium oxide. Scanning electron microscope (SEM) and transmission electron microscopy (TEM) were used to determine the morphology of products. Ultraviolet–visible spectroscopy (UV–Vis) was used for determining optical properties.

2. Materials and methods

2.1. Chemicals and materials

Representative samples of a chromium slag were obtained from Shenhong Co., Ltd. Xinjiang, China. The chromium slag is aluminum dregs containing chromium (VI) which produced in the chromic salt production. All chemical reagents were analytical grade without further purification and purchased from Sinopharm Chemical Reagent Co., Ltd., China. The muffle furnace (HY-1200 °C) was purchased from Changsha Shunze mining and metallurgy machinery manufacturing Co., Ltd., China. Reaction kettle was obtained from Dalian Fuyang Science and Technology Development Co. Ltd., China. Electrolytic tank and cation-exchange membrane used were supported by Steel Vanadium & Titanium Co. Ltd., China. Power was supplied by Beijing Zhaoxin information technology Co. Ltd., China. CO_2 was from Guangming Special Gas Co. Ltd., Dalian, China. Sodium ionometer was purchased from Shanghai Rex Co. Ltd., China.

2.2. Instrumental analysis

Thermogravimetric analysis (TGA) was applied under program control temperature to measure the quality of the material along with the change of temperature (or time). Thermogravimetric measurements and differential thermal analysis were performed with a Perkin Elmer Diamond thermogravimetric differential thermal analyzer. The sample was placed in a platinum sample holder. Measurements in air with a flow rate of 100 mL min^{-1} were carried out over a temperature range of 30–1000 °C with heating rate of 10 °C min^{-1}. X-ray diffraction (XRD) patterns were recorded using X-ray diffractometer (DX 2000 China), using Cu-Kα radiation ($\lambda = 1.5406$ Å) with a tube voltage of 40 kV and 20 mA with 2θ ranges from 20° to 90°, with a step size of 0.01° and a step time of 0.3 s. Scanning electron microscope (SEM) analysis was carried out by using Scanning Electron Microscope (JEOL-JSM-5600 LV Japan). For this purpose the catalysts were mounted on the sample stubs and coated with gold foil using gold coating machine (JEOL-JSM-420, Japan). The low resolution transmission electron microscopy (TEM) images were obtained by an H-7500 transmission electron microscope (Hitachi, Japan), using an accelerating voltage of 100 kV. The high resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) patterns were taken from a TECNAI G2 transmission electron microscopy (FEI, Netherlands) with an accelerating voltage of 200 kV. All samples were prepared on a lacey carbon film supported by a copper grid. Ultraviolet–visible spectroscopy (UV–Vis) spectrum was recorded on a SolidSpec 3700DUV UV-VIS-NIR spectrophotometer (Shimadzu, Japan) equipped with an integrating sphere at room temperature.

2.3. Experimental study

2.3.1. Preparation of chromium oxide

Sodium dichromate solution was obtained by leaching chromium (VI) waste resource with deionized water and primary separation. Fig. 1 shows the scheme of synthesizing chromium oxide. The electrolytic tank was separated into anode compartment and cathode compartment by cation exchange membrane. Then, sodium dichromate solution was added into the anode compartment and sodium hydroxide solution was added into the cathode