Converting Waste Polyethylene into ZnCCo₃ and ZnCNi₃ by a One-Step Thermal Reduction Process

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ABSTRACT: Plastic products have brought us great convenience in our daily life and work. But in the meantime, waste plastics have become solid pollutants in the environment due to its poor degradability. The resource utilization of waste plastic can decrease environmental pollution. Here, a thermal reduction method for the conversion of waste polyethylene to ZnCCO₃ and ZnCNi₃ in a stainless-steel autoclave under mild conditions has been reported. X-ray powder diffraction patterns indicate that the obtained samples are anti-perovskite-structured ternary carbides (ZnCCO₃ and ZnCNi₃) with good crystallinity. Moreover, the formation mechanism of ternary carbides has been briefly discussed. This method can be developed into an effective method for disposal of other waste plastics.

1. INTRODUCTION

Since the remarkable discovery of superconductivity at 8 K in MgC₅Nₙ, the anti-perovskite-structured compounds (ternary carbides and nitrides) have attracted great attention due to their excellent physical properties such as giant magnetoresistance effects, negative thermal expansion, nearly zero temperature resistivity coefficient, giant barocaloric effects, magnetostriiction, spin-glass behavior, phase separation, and magnetocaloric effect.

Up to now, considerable efforts have been made to explore new methods to synthesize ternary carbides with anti-perovskite structure, including repeated sintering, self-propagating high-temperature synthesis, the mechanical alloying method, and conventional powder metallurgy. Xia and co-workers have synthesized MgCNi₃ bulk materials at 850 °C for several tens of minutes through a hybrid microwave heating method. Single crystalline MgCNi₃ of several hundred micrometers in size can also be successfully synthesized by heat treatment of a mixture of carbon, metallic Mg, and Ni powders under high-pressure (4.25 GPa) conditions at 1200 °C for 1 h. Rana and co-workers have synthesized ternary carbides (MgCNi₃ or Mg₃C₂N₃) encapsulated in carbon nanoflask by using metallic Mg–EtOH powder and Ni(CO)₅ or cobalt tricarboxyl nitrosyl as starting materials at 1000 °C for 3 h. You and co-workers have synthesized NiO nanorods, monolayer graphene, and SiC nanowires from waste materials through a green chemical vapor method. Some efforts have been made to convert waste plastics into valuable carbon-based materials. Different forms of carbon materials have been prepared by utilizing waste plastic (poly(ethylene terephthalate), poly(tetrafluoroethylene), polyethylene (PE), etc.) as a carbon source.

Plastic products have been used widely in the industrial fields and in daily life due to their excellent properties such as light, high transparency, low cost, durability, and good corrosion resistance. However, solid pollutants caused by waste plastics have become more and more serious with the increasing use of plastic products. Thus, resource utilization of waste plastics is helpful for environmental protection. Recently, some effort has been made to convert waste plastics into valuable carbon-based materials. In this paper, a facile procedure for the preparation of ZnCCO₃ and ZnCNi₃ by a chemical reaction under mild conditions has been reported.

Plastic products have been used widely in the industrial fields and in daily life due to their excellent properties such as light, high transparency, low cost, durability, and good corrosion resistance. However, solid pollutants caused by waste plastics have become more and more serious with the increasing use of plastic products. Thus, resource utilization of waste plastics is helpful for environmental protection. Recently, some effort has been made to convert waste plastics into valuable carbon-based materials. Different forms of carbon materials have been prepared by utilizing waste plastic (poly(ethylene terephthalate), poly(tetrafluoroethylene), polyethylene (PE), etc.) as a carbon source. Plastic waste can also be used as a carbon source to prepare carbide materials (SiC, TiC, ZrC, VC, NbC, Cr₂C₃, Cr₂AlC, etc.). You and co-workers have synthesized NiO nanorods, monolayer graphene, and SiC nanowires from waste materials through a green chemical vapor method. The above approaches of converting waste plastic to valuable materials can deliver important significance in environmental protection.
Herein, a one-step thermal reduction process is designed to produce ZnCCo\textsubscript{3} and ZnCNi\textsubscript{3} by using waste PE as a carbon source in a stainless-steel autoclave at 800 °C. This study provides a simple and effective route for converting waste plastics into high-value carbide materials. The reaction temperature used in our method for the production of ternary carbides is lower than those of the reported methods.

2. RESULTS AND DISCUSSION

The Fourier transform infrared (FTIR) spectrum was used to investigate the chemical structure of waste plastic bags. From the FTIR spectrum (Figure 1), the main chemical composition was high-density polyethylene. The phase structure and purity of the obtained sample were investigated by X-ray powder diffraction (XRD). Figure 2 shows the XRD pattern of the ZnCCo\textsubscript{3} sample. Three diffraction peaks in the XRD pattern located at 2θ = 41.97, 48.91, and 71.61° could be indexed as the (111), (200), and (220) diffraction planes of the cubic phase ZnCCo\textsubscript{3} with a lattice constant of a = 3.734 Å, which is in agreement with the reported data (JCPDS cards No. 29-0524, a = 3.730 Å). All of the above results prove that the obtained sample is anti-perovskite-structured ZnCCo\textsubscript{3}. The yield of ZnCCo\textsubscript{3} is calculated to be about 56%, according to the quality of ZnCCo\textsubscript{3} and raw material (metallic cobalt).

The morphology, microstructure, and composition of the obtained ZnCCo\textsubscript{3} sample were further investigated with scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and energy-dispersive X-ray (EDX). The SEM image of the obtained ZnCCo\textsubscript{3} sample is shown in Figure 3a, which reveals that the ZnCCo\textsubscript{3} sample is composed of particles with different sizes. A typical TEM image (shown in Figure 3b) shows that the size of ZnCCo\textsubscript{3} particles is in the range of 50–200 nm. The HRTEM image (shown in Figure 3c) shows that the crystal lattice spacing of 0.37 nm corresponds to the d spacing values of the (100) and (010) planes of cubic phase ZnCCo\textsubscript{3}. A typical selected-area electron diffraction (SAED) pattern of the obtained ZnCCo\textsubscript{3} particles (inset of Figure 3c) recorded along the (001) zone axis confirms that the obtained ZnCCo\textsubscript{3} particles are well crystalline, and the diffraction spots can be indexed to the diffractions of cubic phase ZnCCo\textsubscript{3}, which is close to the result of the XRD pattern (Figure 2). The EDX spectrum taken from the obtained ZnCCo\textsubscript{3} particles is shown in Figure 3d, which shows intense peaks of C, Cu, Zn, and Co. The Cu signals come from the TEM grid. The EDX spectrum indicates that the obtained ZnCCo\textsubscript{3} particles consist of C, Zn, and Co.

All of the three diffraction peaks in Figure 4 (XRD pattern of the obtained ZnCNi\textsubscript{3} sample) located at 2θ = 42.88, 49.93, and 73.27° could be indexed as the (111), (200), and (220) planes of anti-perovskite-structured ZnCNi\textsubscript{3} with a lattice constant of a = 3.650 Å, which is consistent with the earlier report by Park and co-workers (a = 3.660 Å). The yield of ZnCNi\textsubscript{3} is calculated to be about 68%, according to the quality of ZnCNi\textsubscript{3} and raw material (metallic nickel). SEM image and TEM image are shown in Figure 5a,b, respectively, which clearly show that the ZnCNi\textsubscript{3} sample consists of nanoparticles with an average particle size of 40 nm.

The magnetic behavior is of great importance for the practical applications of materials. The magnetic properties of the ternary carbides were investigated at room temperature. The magnetic hysteresis curves for the obtained ZnCCo\textsubscript{3} and ZnCNi\textsubscript{3} samples are shown in Figure 6a,b, respectively. The
In our present approach to synthesize the anti-perovskite-structured ternary carbides, a possible formation mechanism is proposed. With the temperature increasing, metallic sodium reacts with zinc chloride to produce nascent zinc (Zn*) and sodium chloride (eq 1) Meanwhile, waste PE decomposed generating nascent carbon (C*) and H₂ (eq 2). The nascent Zn and nascent C (with high reactivity) can react with transition metal (cobalt or nickel) to produce ternary carbides (ZnCCo₃ or ZnCNi₃) at a low temperature of 800 °C [eq 3].

Based on free-energy calculations, reaction 1 is thermodynamic, spontaneous (ΔG°m = −379.28 kJ/mol), and highly exothermic (ΔH°m = −405.93 kJ/mol). From the ΔH°m value of reaction 1, it can be seen that a large amount of heat has been generated from reaction 1, which is conducive to the formation of ternary carbides at low temperature. Therefore, the possible formation process of MgCNi₃ can be described as follows

\[
2\text{Na} + \text{ZnCl}_2 \rightarrow 2\text{NaCl} + \text{Zn}^* \\
1/n[\text{CH}_3]_n \rightarrow \text{C}^* + \text{H}_2 \\
\text{Zn}^* + \text{C}^* + 3\text{M} \rightarrow \text{ZnCM}_3 (M = \text{Co or Ni})
\]

All of the total reaction process could also be represented as follows

\[
\text{ZnCl}_2 + 1/n[\text{CH}_3]_n + 3\text{M} + 2\text{Na} \\
\rightarrow 2\text{NaCl} + \text{H}_2 + \text{ZnCM}_3 (M = \text{Co or Ni})
\]

3. CONCLUSIONS

In this study, anti-perovskite-structured ZnCCo₃ and ZnCNi₃ have been successfully synthesized by a facile one-step chemical reaction at a relatively low temperature of 800 °C. This work provides an effective method to convert waste PE to valuable ternary carbide with anti-perovskite structure. The magnetic behaviors of the obtained samples have been briefly investigated. This synthesis method can be applied to prepare other ternary carbides.

4. EXPERIMENTAL SECTION

4.1. Reagents. Waste polyethylene used in our experiments was recovered from plastic bags (main components: PE). All of the other reagents were of analytical purity and purchased from Sinopharm Chemical Reagent Co., Ltd.

4.2. Preparation of ZnCCo₃ Particles. In a typical synthesis process, zinc chloride (2.70 g), cobalt metal (1.80 g), waste polyethylene (1.00 g) and sodium metal (2.00 g) were added into a stainless-steel autoclave of about 20 mL capacity. After sealing tightly, the autoclave was heated in an electronic furnace from room temperature to 10 °C/min at 800 °C and maintained at 800 °C for 10 h. After the autoclave was naturally cooled to room temperature, a black sample was collected from the autoclave and washed with anhydrous alcohol to remove excess metallic sodium. The sample was then washed with diluted hydrochloric acid and distilled water to remove other impurities. Finally, the obtained sample was dried at 50 °C under vacuum for further identification.

4.3. Preparation of ZnCNi₃ Nanoparticles. The experimental procedure for the preparation of ZnCNi₃ is similar to that employed to produce ZnCCo₃ except that metallic cobalt was substituted by metallic nickel (1.80 g). The preparation procedures are summarized diagrammatically in Scheme 1.

4.4. Samples’ Characterization. The phase of the obtained samples was investigated by X-ray powder diffraction (XRD), using a Philips X’Pert X-ray diffractometer (Cu Ka λ = 1.54178 Å). The microstructures of the obtained samples were derived from scanning electron microscopy images (FESEM, JEOL-JSM-6700F). The magnetic hysteresis loop was determined by a vibrating sample magnetometer (VSM, BHV-SS). Transmission electron microscopy (TEM) image, high-resolution transmission electron microscopy (HRTEM) image, selected-area electron diffraction (SAED) pattern, and
energy-dispersive X-ray spectrum (EDX) analysis were carried out on a JEOL-2010 transmission electron microscope (at an accelerating voltage of 200 kV). The magnetic properties were investigated on a SQUID magnetometer.

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**Notes**

The authors declare no competing financial interest.

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