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One-step chemical synthesis of MgCNi3 nanoparticles embedded in carbon nanosheets utilizing waste polyethylene as carbon source

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Abstract

MgCNi3 nanoparticles embedded in carbon nanosheets have been successfully synthesized from waste polyethylene (PE) by one-step chemical reaction at a relatively low temperature of 800 °C. X-ray diffraction pattern indicates that the obtained sample is anti-perovskite structured MgCNi3. Transmission electron microscopy image shows that MgCNi3 nanoparticles are embedded in the carbon nanosheets. Magnetization measurement shows that the obtained sample has a superconducting transition at 6.8 K. This method is not only to develop an effective method to synthesize MgCNi3 superconductor under mild conditions but also to provide a novel technique to convert waste polyethylene to valuable carbide materials.

1. Introduction

The anti-perovskite structured compounds have attracted attention since the remarkable discovery of superconductivity at about 8 K in MgCNi3 [1]. In the past years, ternary carbides and nitrides with the anti-perovskite structure have been extensively investigated for their excellent properties, such as giant magnetoresistance effect [2, 3], nearly zero temperature resistivity coefficient [4–6], giant barocaloric effect [7], magnetostriiction [8], negative thermal expansion [9], phase separation [10], magnetocaloric effect [11], and spin-glass behavior [12–15].

Since He and co-workers first prepared the superconductor MgCNi3 from the mixture of bright Mg flakes, nickel powder and glassy carbon spherical powder through repeated sintering [1], several synthetic methods for producing MgCNi3 have been reported. MgCNi3 has been synthesized by self-propagating high-temperature synthesis (SHS) technique followed by an isothermal treatment at 1123 K under an inert Ar atmosphere [16]. MgCNi3 can also be obtained from Mg (or Mg2Ni), metallic nickel and graphite powders by mechanical alloying (MA) method [17]. MgCNi3 superconductor bulk materials have been synthesized by using carbon nanotubes as carbon source via the conventional powder metallurgy [18]. Xia and co-workers have synthesized MgCNi3 bulk materials using a hybrid microwave heating method at 850 °C for several tens of minutes [19]. The single crystalline MgCNi3 of several hundred micrometers in size can also been successfully synthesized by heat treatment of the mixture of Mg, C, and Ni powders under high-pressure (4.25 GPa) conditions at 1200 °C for 1 h [20]. MgCNi3 particles encapsulated in carbon nanolaks have been synthesized by using metallic Mg-EtOH powder and Ni(CO)3 as starting materials at 1000 °C for 3 h [21]. However, many of the above synthesis methods require multi-step process and high reaction temperature. Therefore, to explore a one-step method to synthesize MgCNi3 is still a challenging subject.
Plastics has become an indispensable part of everyday life for their excellent properties such as durability, light, low toxicity, low cost, and resistance to corrosions. However, waste plastic has become solid pollutants in environment for its poor degradability. Thus, to develop an effective technology for the recycling of waste plastic is highly necessary. Recently, many studies have been reported to convert waste plastics to valuable carbon with varied morphologies such as nanoparticles, onion-like carbon microspheres, nanotubes, and metal-carbon composites [22–30]. Our group recently has developed an effective method to convert waste plastic (PE, PVC, and PTFE) to carbides under mild conditions [31–37]. Efficient HER electroncatalysts based on metal-carbon composites have been synthesized from electronic waste or resin [38–42]. In this study, MgCNi3 nanoparticles embedded in carbon nanosheets have been synthesized by using waste PE, metallic Na, magnesium chloride and metallic nickel as starting materials at 800 °C. The purpose of this work is not only to develop one-step chemical reaction method to synthesize MgCNi3 superconductor, but also to provide a novel technique to convert waste PE to valuable materials.

2. Experimental

Magnesium chloride (chemically pure, 99%) used in our experiments was purchased from Shanghai Macklin Biochemical Co., Ltd. All of the other raw materials (such as metallic Na, metallic nickel, and absolute ethyl alcohol) were purchased from Sinopharm Chemical Reagent Co., Ltd. Waste PE was obtained from waste plastic bags. First, waste plastic bags (waste PE) were washed with water, and were cut into small pieces to facilitate loading. Subsequently, metallic nickel (1.80 g), magnesium chloride (1.60 g), waste PE (1.00 g), and excess metallic sodium (2.00 g) were put into a stainless steel autoclave (the volume of the autoclave is about 20 ml). After closing tightly, the autoclave was heated in an electronic furnace. Then, the temperature of the electronic furnace was increased from room temperature to 800 °C at a rate of 10 °C/min and kept at 800 °C for 10 h. After the autoclave was allowed to cool down to room temperature naturally, the black product was collected from the autoclave. The obtained raw product was washed with alcohol, distilled water, and dilute HCl for several times, respectively, to remove the by-product and unreacted raw materials. After drying under vacuum 60 °C for several hours, the final black powder was collected for further characterization. XRD measurement was carried out with a Philips X-pert x-ray diffractometer (CuKα = 1.54178 Å). The morphology of the obtained samples was studied by scanning electron microscopy (SEM, JEOL-JSM-6700F) and transmission electron microscopy (TEM, H7650). High-resolution transmission electron microscopy (HRTEM) image was obtained on transmission electron microscope (a JEOL-2010) with selected-area electron diffraction (SAED) pattern attached. The magnetization measurements were carried out at 2–20 K and at 10 Oe using a SQUID magnetometer (MPMS, Quantum Design).

3. Results and discussion

The structure of the obtained sample is investigated by powder x-ray diffraction. A typical powder XRD pattern of the obtained sample is shown in figure 1. The six diffraction peaks located at 2θ = 23.30°, 33.21°, 41.08°, 47.67°, 53.74°, and 69.74° in figure 1 could be indexed as the (100), (110), (111), (200), (210), and (220) diffraction planes of the anti-perovskite structured MgCNi3, with lattice constant of a = 3.813 Å, which is in agreement with the reported value (JCPDS cards No. 41-0903, a = 3.816 Å). The peak located at 2θ = 26.50° can be indexed as the (002) diffraction plane of hexagonal graphite. All the above results prove that the obtained sample is composed of carbon and MgCNi3.

The morphology and microstructure of the obtained sample are further investigated by SEM, TEM, and HRTEM. SEM image of the obtained sample is shown in figure 2(a), which reveals that the sample is composed of carbon nanosheets. A typical TEM image (figure 2(b)) shows that MgCNi3 nanoparticles with a size of 20–100 nm are embedded in the carbon nanosheets. The HRTEM image (shown in figure 2(c)) shows that the crystal lattice spacings are about 0.38 nm, corresponding to the interplanar (010) and (100) distances of MgCNi3, respectively. A typical SAED pattern is shown in figure 2(d), which records along the <001> zone axis. The diffraction spots could be indexed to the diffractions of anti-perovskite structured MgCNi3, which is consistent with the XRD pattern. It confirms that the obtained MgCNi3 nanoparticles are well crystalline.

Magnetization measurements on MgCNi3 nanoparticles embedded in carbon nanosheets are measured at 2–20 K and at 10 Oe with SQUID. Magnetization as a function of temperature (M–T curve) is shown in figure 3. The superconducting transition temperature (Tc) of the obtained sample is determined by magnetization measurement under conditions of zero field cooling (ZFC) and field cooling (FC) at 10 Oe. The clear onset of a strong Meissner effect can be observed, which indicates that the Tc for the obtained sample is 6.8 K. The diamagnetism signal observed in the FC measurement is obviously weaker than that in the ZFC measurement.
This $T_c$ of 6.8 K is a little lower than the highest of 7.4 K for polycrystalline MgC$_x$Ni$_3$ ($x = 1.5$) [1], which may originate from the lower carbon stoichiometry in the obtained sample.

In our experiments, waste plastic bags decompose generating carbon and H$_2$ with the temperature increasing (equation (1)). The molten MgCl$_2$ (melting point, 714 °C) is then reduced by metallic sodium to Mg (equation (2)) at the reaction temperature of 800 °C. The newly formed Mg and C atoms have reacted with metallic nickel to produce MgCNi$_3$ at a low temperature of 800 °C (equation (3)). When metallic Mg is used to replace metallic Na and MgCl$_2$ as raw materials, MgCNi$_3$ cannot be produced from the reaction of waste plastic bags, metallic Ni and Mg at 800 °C through similar process. This may be because the newly formed Mg atoms have highly reactive. In addition, the reaction (equation (2)) is thermodynamically spontaneous ($-164.80$ kJ mol$^{-1}$) and exothermic ($-180.83$ kJ mol$^{-1}$) according on the calculations of free energy. A large amount of heat generated from the reaction (equation (2)) is benefit to the formation of MgCNi$_3$ at reaction temperature. Therefore, the possible formation process of MgCNi$_3$ has been described as follows:

$$\frac{1}{n}[\text{CH}_2]_n = \text{C} + \text{H}_2 \quad \text{(1)}$$
$$2\text{Na} + \text{MgCl}_2 = \text{Mg} + 2\text{NaCl} \quad \text{(2)}$$
$$\text{C} + 3\text{Ni} + \text{Mg} = \text{MgCNi}_3 \quad \text{(3)}$$

Figure 1. A typical XRD pattern of the obtained sample.

Figure 2. (a) SEM image of the obtained sample; (b) A typical TEM image of the obtained sample; (c) HRTEM image of the obtained sample; (d) SAED pattern along the (001) zone axis.
All the total reaction process can be represented as follows:

$$2\text{Na} + \frac{1}{n}\text{CH}_2\text{I}_n + 3\text{Ni} + \text{MgCl}_2 = \text{MgCNi}_3 + 2\text{NaCl} + \text{H}_2$$

4. Conclusion

In conclusion, MgCNi$_3$ nanoparticles embedded in carbon nanosheets have been successfully and directly synthesized from waste PE by a facile one-step chemical reaction. The obtained MgCNi$_3$ particles are well protected by the carbon nanosheets that have not affect the superconducting properties of the MgCNi$_3$ nanoparticles. This simple approach takes advantage of using waste PE as carbon source, simple apparatus, and low reaction temperature. Furthermore, it could provide a new method to deal with waste plastics.

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Figure 3. Temperature dependence of magnetization for the obtained sample.
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