Journal of Molecular Structure 1175 (2019) 496–503

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

In situ synthesis of chromium carbide nanocomposites from solution combustion synthesis precursors

Zhiqin Cao*, Chengyang Zuo

School of Materials Engineering, Pan Zhihua University, Pan Zhihua, 617000, China

ARTICLE INFO

Article history:
Received 8 April 2018
Received in revised form
31 July 2018
Accepted 5 August 2018
Available online 7 August 2018

Keywords:
Chromium carbide
Synthesis
Nanorods
Carbonization

ABSTRACT

Chromium carbide nanocomposites were in situ synthesized by combing solution combustion synthesis method and carbothermal reduction for the first time. A homogeneous precursor (amorphous chromium oxide and carbon) was fabricated by solution combustion synthesis method using glucose, chromium nitrate and glycine as raw materials. The precursor powders were subsequently reduced under nitrogen at 600–900 °C for 1 h. The combustion synthesis process and carbothermal reduction process were studied in detail. The products were analyzed by X-ray diffraction, scanning electron microscope and energy dispersive spectrometer, field-emission electron microscope, transmission electron microscopy, high-resolution transmission electron microscopy and Raman spectrometer. The results indicated the chromium carbide nanorods with well crystalline structure were successfully in situ synthesized at low temperature (700 °C) without any catalyst. When further improved the temperature, the carbon in the products transformed into graphite and chromium carbide is gonging to allotropic transformation. Furthermore, it can prepare graphite based nanosheet composites at lower temperatures (900 °C).

1. Introduction

As the most stable transition metal carbide, chromium carbide (Cr_3C_2) is being given significant attention because of their excellent strength, hardness, Young's modulus, oxidation resistance, corrosion properties and permanent non-magnetizability [1–6]. Therefore, it has been widely used in a variety of industrial applications, such as shaft bearings, seals, high-temperature furnaces, nozzles, electrical discharge machining, molds and catalyst [7–9].

Various methods for synthesis chromium carbide have been investigated, including mechanical thermal synthesis [10,11], chemical vapor deposition [12], arc discharge [13], gas reduction carburization [14,15] and so on. However, industrial applications of these methods still limited due to the time consuming (multi-steps to remove the by-products), high cost and high temperature (>1400 °C) [16,17]. Finding a procedure with cost effective is a desired goal of material field. Herein, we describe a simple and versatile new strategy for producing chromium carbide (Cr_3C_2) by combining the combustion synthesis method and carbothermal reduction process. We used chromium nitrate, glycine and glucose as starting materials; the precursors were prepared by solution combustion synthesis method in several minutes. The combustion reaction was activated at 300 °C on an electrical furnace. Then, the precursors were carbonized in tube furnace with inert atmosphere. This method has presented many advantages. First, the apparatus are simple and the raw materials are inexpensive. Second, the combustion reaction is a exothermic, a relatively low temperature is required to activate the reaction, and the combustion can then continue without extra energy supply. Third, the raw materials are mixing at the molecular level, a simple synthesis process can prepare fine and highly homogeneous powder precursors with mesoporous structure, and the metal source and carbon source are contacted intimately. Research indicated that one of the major problems with traditional solid-state synthesis was slow diffusion between solids and many methods still use extremely high temperatures to increase the rate of diffusion [18]. Compare to the traditional methods, because of the intimately contacted of chromium source and carbon source, the distance of diffusion decreases and the rate of diffusion increases. The precursor exhibits a higher activity, thus resulting preparation chromium carbide nanoparticles at lower temperature and shorter reaction time without any catalyst.

* Corresponding author.
E-mail address: cao_zhi_qing@163.com (Z. Cao).

https://doi.org/10.1016/j.molstruc.2018.08.008
0022-2860/

2. Experimental

2.1. Synthesis

The glucose ($C_6H_{12}O\cdot H_2O$), chromium nitrate ($Cr(NO_3)_3\cdot 9H_2O$) and glycine (NH_2CH_2COOH) were used as starting materials. All the chemicals are at least reagent grade and used as received without further purification. Starting materials (10 g chromium nitrate, 6 g glycine and glucose) were dissolved into 500 ml glass with deionized water to prepare precursor by SCS. During the experiments the ratio between glucose and chromium nitrate (G/Cr), ϕ, is 0.5, 1 and 1.5, which labeled as I, II and III, respectively. The experimental process has been previously demonstrated in detail elsewhere [19]. The carbonization of precursor was performed in a tube furnace. A strict temperature program was followed in all runs, with heating rate of 10 K min^{-1}. The precursors were carbonized in N_2 atmosphere at various temperatures (600 °C, 700 °C, 800 °C, 900 °C) for 1 h and cooled to room temperature naturally. The flow rate of Ar was 1 L/min.

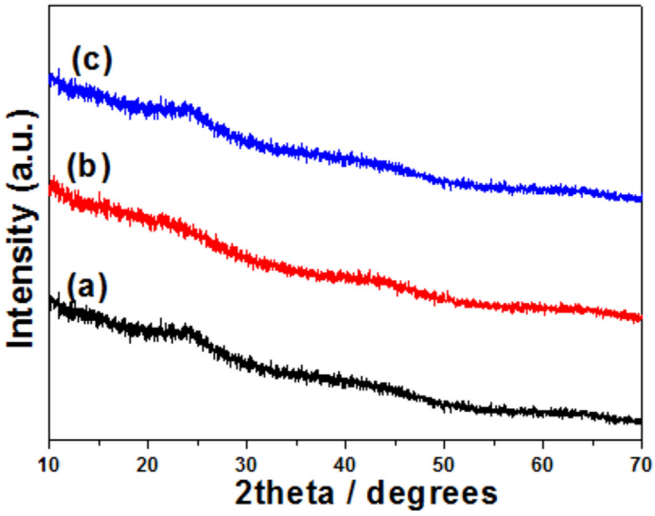

Fig. 1. XRD patterns of the precursors: (a) I precursor, (b) II precursor (c) III precursor.

2.2. Characterizations

The precursors and carbonization products were analyzed by X-ray diffractometer [(X-ray diffraction (XRD), Cu-K_α radiation ($\lambda = 0.1542$ nm), Rigaku, D/max-RB12]. The reaction process was characterized thermogravimetry (TG)-differential scanning calorimetry (DSC) coupled with a mass spectrometer. The morphology of products were observed by scanning electron microscopy (SEM, JSM-5600), field-emission electron microscope (Tecnai G2 F30 S-TWIN), transmission electron microscopy (TEM, Tecnai G2 F30 S-TWIN) and high-resolution transmission electron microscopy (HRTEM). The Raman spectra was analyzed on a microscopic confocal Raman spectrometer (Renishaw RM2000) using Ar^+ laser excitation with a wavelength of 514.5 nm.

3. Results an discussion

Fig. 1 shows the XRD patterns of the precursors. It is evident that

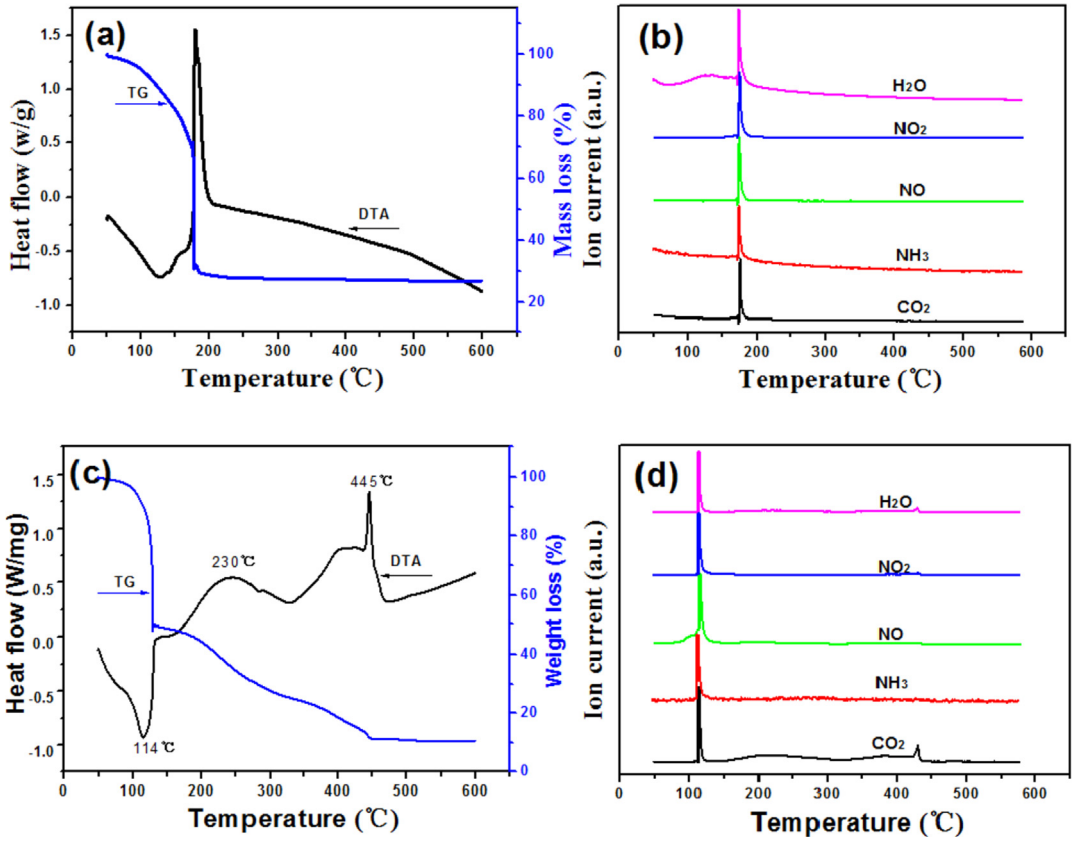

Fig. 2. Results of (a)TG–DSC and (b) MS analysis for the reaction of the glycine and chromium nitrate; results of (c)TG–DSC and (d) MS analysis for the reaction of the glycine, chromium nitrate and glucose.