



Shape-controlled syntheses of Co_3O_4 nanowires arrays with excellent catalytic performances upon ammonium perchlorate decomposition



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ABSTRACT

Co_3O_4 nanowires (NWs) arrays were successfully fabricated via a facile hydrothermal-annealing method. The component, structure and morphology of the Co_3O_4 NWs arrays were characterized. The slim Co_3O_4 NWs consist of interconnected nanocrystals and have a specific surface area of $26.6 \text{ m}^2 \text{ g}^{-1}$. The obtained materials have exhibited an excellent catalytic performance on the thermal decomposition of ammonium perchlorate (AP). In addition, catalytic activities of the prepared Co_3O_4 mainly depend on the content of catalyst. Impressively, an addition of 9 wt% Co_3O_4 NWs arrays to AP exhibited the most significant catalytic effect in lowering the decomposition temperature from 404 to 288 °C, increasing the decomposition heat from 502 to 930 J g^{-1} and decreasing the activation energy from 201 to 168 kJ mol^{-1} . Furthermore, the catalytic mechanism of the Co_3O_4 NWs arrays based on electron transfer processes was discussed.

1. Introduction

Nowadays, composite solid propellants have drawn tremendous attentions and widely been used in aerospace, universal exploration, satellite launching, ballistic missile and other assist propulsion [1–4]. NH_4ClO_4 or AP is the crucial energetic material and main oxidizing agent used in composite solid propellants (ca. 60–90 wt% of the whole propellant). More importantly, its thermal decomposition characteristics play a key role in the combustion behavior of the propellants [5–9]. The low thermal decomposition temperature and high exothermic heat of AP will be accompanied by the short ignition delay time and high burning rate of the propellants [10–12]. Thus, considering the security and the limited loading of AP in propellants, it is desirable to improve the decomposition efficiency of AP in order to generate high energy at low burning temperature. Recently, numerous nano-sized transition metal oxides, including CuO, Fe_2O_3 , Co_3O_4 , CoO, MnO_2 etc., have been evaluated for the catalytic performances upon AP decomposition [13–22]. However, the catalytic properties of nano metal oxides for the thermal decomposition of AP vary from different morphologies and microstructures [23–25]. Therefore, to develop shape-controlled nanocatalysts applied in the thermal decomposition of AP still remains a great challenge.

Co_3O_4 , as one of the important transition metal oxides and intrinsic p-type semiconductors [26,27], has attracted considerable attentions as

a potential catalyst for the thermal decomposition of AP [25,28–30]. Currently, significant research efforts have been made to design and synthesize Co_3O_4 with diverse morphologies and structures owing to their notable improvement in catalytic performances [8,31–33]. For example, Alizadeh et al. have prepared spherical Co_3O_4 nanostructure via sol-gel method, which could facilitate the decomposition of AP [28]. Sun et al. have reported the comparative investigations of the catalytic behaviors of Co_3O_4 nanocrystals with different morphologies (including flower-like architectures, multilayer stacked structures and nanosheets) for the thermal decomposition of AP [23]. Results show that the large specific surface area and pore volume lead to the high catalytic activity. In addition, Zhang et al. have successfully synthesized Co_3O_4 nanoflakes and urchin-like Co_3O_4 using the thermal decomposition of different precursor approaches, respectively [32,34]. Both catalysts reveal the significant enhancement effect on the decrease in the decomposition temperature of AP. Although the catalytic applications of the Co_3O_4 with diverse morphologies have been widely studied, the one-dimensional (1D) Co_3O_4 NWs as a catalyst for the thermal decomposition of AP has been rarely documented. The synthesis of Co_3O_4 NWs in a controlled manner is a critical step [24]. Vertically aligned Co_3O_4 NWs arrays are regarded as the interesting candidate used in the thermal decomposition of AP due to their morphological controllability, large surface area as well as effective transportation of electrons [35–37].

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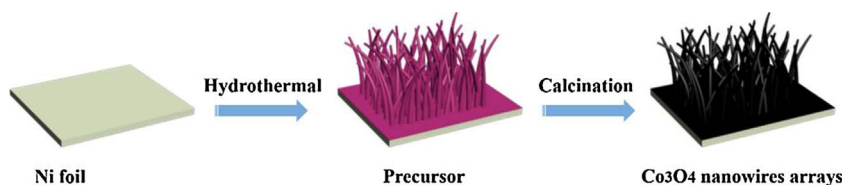


Fig. 1. Schematic illustration of the preparation process of the Co_3O_4 NWs arrays.

Herein, we propose a relatively simple hydrothermal and post-treatment method for the synthesis of 1D Co_3O_4 NWs arrays. The possible formation mechanism has been discussed. The component, structure and morphology of the as-obtained Co_3O_4 have been investigated. Furthermore, the thermal decomposition of AP with the Co_3O_4 NWs arrays as catalysts has been studied in detail to exhibit their outstanding role in speeding AP breakdown.

2. Experimental

2.1. Chemicals and materials

Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%), urea ($\text{CO}(\text{NH}_2)_2$, 99.5%), ammonium fluoride (NH_4F , 96%), anhydrous ethanol (99.7%), acetone (99.5%), Ni foil (99.5%) and NH_4ClO_4 (99.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Co_3O_4 nanoparticles (Co_3O_4 NPs, 99.9%) with an average size of 30 nm were supplied by Aladdin Industrial Corporation. All chemicals were of analytical grade and used as received without any further purification. Prior to the synthesis, the Ni foil ($4 \times 2 \times 0.1 \text{ cm}^3$) was ultrasonically cleaned by acetone, ethanol, and deionized water in sequence for 15 min each.

2.2. Synthesis of Co_3O_4 NWs arrays

Co_3O_4 NWs arrays were directly grown on Ni foil by a hydrothermal and next annealing procedure according to the previous reports with some modifications [38–40]. In detail, 5 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 10 mmol of NH_4F , and 25 mmol of urea were completely dissolved in 50 mL distilled water under a constant magnetic stirring. This homogeneous solution was transferred into a 50 mL Teflon-lined stainless steel autoclave. A piece of pre-cleaned Ni foil was then immersed into the above reaction solution. After that, the autoclave was sealed and maintained at 120°C for 5 h in an electron oven, and cooled down to room temperature naturally after hydrothermal reaction. Then, the pink precursor was taken out and rinsed with distilled water to remove the residual reactant. Finally, the precursor was annealed in air at 400°C for 4 h to obtain as-prepared Co_3O_4 NWs arrays.

2.3. Synthesis of Co_3O_4 NWs arrays/AP composites

Before the experiments, Co_3O_4 NWs arrays need to be scraped from the Ni foil. AP and the as-obtained Co_3O_4 were mixed at the different weight ratios and ground carefully in an agate mortar for 30 min, and then the mixtures were dried at 50°C . For comparison, the catalytic property of Co_3O_4 NPs and thermal decomposition measurement of pure AP without Co_3O_4 were also investigated.

2.4. Characterizations

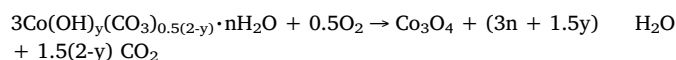
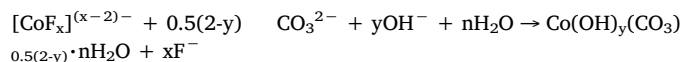
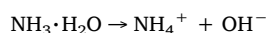
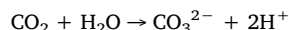
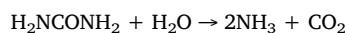
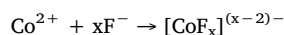
X-ray diffraction (XRD) patterns of the obtained materials were acquired using a Bruker D8 Advance equipped with monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$). Fourier transform infrared (FT-IR) spectra of the samples were recorded with a Nicolet 750 FT-IR spectrophotometer. The X-ray photoelectron spectra (XPS, Thermo ESCALAB 250Xi, $\text{Al-K}\alpha$, 1486.8 eV) were obtained to analyze the chemical composition of the as-prepared Co_3O_4 . The precursor was analyzed by thermogravimetry (TG, Mettler Toledo) from 50 to 500°C . The

morphologies of all the samples were measured with FEI field-emission scanning electron microscope (SEM, Quanta 250F) equipped with an energy dispersive X-ray spectrometer (EDX), transmission electron microscopy (TEM, FEI Tecnai G2 20 LaB6) and high resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 F30 S-Twin). Selected area electron diffraction (SAED) measurements were performed on the TEM. The Brunauer-Emmett-Teller (BET) surface area of samples was measured by physisorption of N_2 at 77 K using a Quantachrome Autosorb-IQ gas adsorption analyzer. The catalytic effect of the as-synthesized Co_3O_4 NWs arrays on the thermal decomposition of AP has been demonstrated by differential scanning calorimetry (DSC, Mettler Toledo) and TG experiments at a heating rate of 20 K min^{-1} in a temperature range of $50\text{--}500^\circ\text{C}$.

3. Results and discussions

3.1. Formation mechanism

A schematic illustration for the whole synthesis process of Co_3O_4 NWs arrays is depicted in Fig. 1. The Ni foil is chosen here as a substrate, which can be replaced by other substrate materials. The entire synthetic procedure of Co_3O_4 NWs arrays could be involved in two main steps: (1) the precursor NWs arrays are perpendicularly formed on the Ni foil by a modified one-pot hydrothermal process. Typically, bivalent Co^{2+} ions are coordinated with F^- to form $[\text{CoF}_x]^{(x-2)-}$ in the as-prepared homogeneous solution. As the reaction temperature rises up to around 70°C , the hydrolysis-precipitation process of urea takes place and generates CO_3^{2-} and OH^- anions, which could help to release Co^{2+} ions from $[\text{CoF}_x]^{(x-2)-}$ and adequately combine with Co^{2+} simultaneously for the formation of nucleus. With the reaction temperature increasing, more and more CO_3^{2-} and OH^- are produced. Many nucleuses form the precursor NWs which subsequently grow directly on the Ni foil substrate. (2) the precursor is converted to the corresponding Co_3O_4 after being annealed at 400°C in air for 4 h, and the morphology features of self-supported NWs arrays are still maintained. The reaction process could be summarized by the following formulas [38,41,42]:



3.2. Physical characterizations

The component and phase structure of the precursor and the final product are examined by XRD measurements shown in Fig. 2. All the reflection peaks of the precursor can be indexed to orthorhombic basic cobalt carbonate hydroxide (JCPDS card No. 48-0083). Followed by a heat treatment, the crystallinity of the product increases. The well-

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