Ceramics International 43 (2017) 16331–16339

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Synthesis and characterization of NiO and Ni nanoparticles using nanocrystalline cellulose (NCC) as a template

Yuan-Teng Foo[a], Joanne Ee-Mun Chan[a], Gek-Cheng Ngoh[b], Ahmad Zuhairi Abdullah[c], Bahman Amini Horri[d,*], Babak Salamatinia[a,*]

[a] Discipline of Chemical Engineering, School of Engineering, Monash University Malaysia, Jalan Lagoon Selatan, Bandar Sunway, 47500 Subang Jaya, Selangor, Malaysia
[b] Department of Chemical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia
[c] School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia
[d] Department of Chemical & Process Engineering, Faculty of Engineering and Physical Sciences, University of Surrey, Surrey GU2 7XH, UK

ARTICLE INFO

Keywords:
Glycine-nitrate combustion
Nanocrystalline cellulose
Nanocomposites
Chemical properties
Transition metal oxides

ABSTRACT

In this study, nanosized nickel oxide (NiO) and nickel (Ni) powders were synthesised via glycine-nitrate (GN) combustion process, assisted by nanocrystalline cellulose (NCC) as a template. Despite the unique morphology of NCC, it has yet to be applied as a sacrificial bio-template for GN combustion process. In addition, NiO and Ni nanoparticles were obtained at relatively low temperatures in this study, whereby the calcination temperatures were varied from 400 °C to 600 °C, with calcination durations of 2, 4, and 6 h. The morphological analysis of the resulting products were conducted using FESEM, which showed uniformly dispersed NiO and Ni particles with average crystallite size of 25 nm and 27 nm, respectively. These results were confirmed using X-ray diffraction (XRD) technique. The Raman and Fourier transform infrared (FTIR) spectra revealed that the molecular fingerprints of the samples were in agreement with each other. Further analyses revealed that samples calcined at 600 °C for 4 h showed the lowest particle size for pure NiO, whereas the lowest particle size for pure Ni was obtained at 400 °C for 4 h. The TGA results were also consistent with the XRD analysis, whereby pure Ni was initially formed and upon heating, had gradually converted into NiO.

1. Introduction

Nanoparticles or nanocomposites have received considerable attention due to their exceptional behaviours and characteristics in terms of quantum size, macroscopic quantum tunnel, large active surface, and high volume [1–4]. Thus, they have diverse applications in catalysis, electronics, photonics, and biomedicine. Transition metals and metal oxides, such as nickel-based nanocomposites have attracted a lot of attention due to their wide range of applications, such as catalysts for biomass pyrolysis and gasification [1,5–11], automotive catalytic converters [12], solid oxide fuel cells (SOFCs) [13], lithium-ion batteries [14], photoelectrochemical solar cells [15–20], electromagnetic fields [21–23], drug delivery applications in the biomedical fields [24,25], optical active filters [26], as well as in the textile industry [27].

Ni-based nanoparticles are functional and effective nanomaterials that demonstrate excellent characteristics as nanocatalysts, primarily due to their effectiveness in different applications. The Ni element in Ni-based nano-catalysts acts as the active site of the catalyst. Therefore, Ni-based nano-catalyst with small particle size and high specific surface area indicates high catalytic performance and efficiency [1,9–11]. Nonetheless, the synthesis route of these metal nanoparticles could affect their morphology and size distribution and consequently, determine their effectiveness [28].

Several general methods to synthesise nanoparticles include solid-state reaction, hydrothermal or solvothermal synthesis, co-precipitation reaction, sol-gel, and solution combustion synthesis. The determining factor for developing single-phase nanoparticles, with high purity and crystallinity is the degree of homogenous mixing of the constituent particles at the atomic level. Homogeneous mixing often requires complicated and complex process controls that could be time consuming and costly [2]. Additionally, pure Ni nanoparticles are often obtained through a two-step process that requires extremely high temperatures of up to 1000 °C. Therefore, the synthesis of high quality nanoparticles is not economically viable in an industrial scale production. In light of these issues, the solution combustion synthesis represents an efficient, simple, and reliable method for producing extremely fine nanoparticles, which do not involve organic solvents and other environmentally unfriendly substances [29]. The glycine-nitrate

* Corresponding authors.
E-mail addresses: b.aminihorri@surrey.ac.uk (B.A. Horri), babak.salamatinia@monash.edu (B. Salamatinia).

http://dx.doi.org/10.1016/j.ceramint.2017.09.006
Received 3 April 2017; Received in revised form 14 August 2017; Accepted 1 September 2017
Available online 06 September 2017

(GN) combustion process is one of the solution combustion synthesis routes, which has several desirable features, such as homogeneous mixing at the molecular level, fast reaction rates, and self-sustaining combustion. The presence of glycine as the fuel improves the level of mixing by forming complexes with the metal ions [2]. However, conventional GN combustion process is extremely vigorous and this limits the kinetics of the transformation process. The process is extremely exothermic that the presence of excess heat can lead to higher fuel consumption and the formation of larger NiO and/or Ni particles. This is due to high temperature sintering or hard agglomeration, which often results in NiO and Ni catalyst of lower specific surface area to volume ratio and lower quality [30,31]. To overcome this issue, previous studies have suggested modifying the solution combustion synthesis process using cellulose [31,32]. In a cellulose-assisted GN combustion process, cellulose helps to sustain the combustion period to ensure the complete combustion reaction of the materials. The confined space formed by the pores in cellulose can also act as a channel for combustion gas emission. Therefore, the combustion products are kept within the cellulose, preventing product loss and pollution to the environment. Metal ions from the oxidizer are protected by the glycine and cellulose structure that form chelating bonds between them, which brings out a space effect from cellulose; hence, the segregation of ions is minimal [31,33]. Several studies have evaluated cellulose-assisted GN process for synthesising nanoparticles that can be applied as catalysts and in SOFCs, but none have applied this process to synthesise NiO and Ni nanoparticles [33–37]. Hence, it is expected that the use of nanocrystalline cellulose (NCC), which is a biodegradable material that exhibits extraordinary fibrous morphology, as the new template in the GN combustion process, would result in NiO and Ni nanoparticles that exhibit extraordinary properties.

Novel NiO and Ni nanoparticles have been synthesised through GN combustion process as reported by Hadke et al. [38], Toniolo et al. [39], and Jegatha Christy and Umadevi [40]. However, to the authors' best knowledge, the application of NCC as the template in a GN combustion process to synthesise NiO and Ni nanoparticles has not been reported. Therefore, this study aimed to synthesise pure NiO and Ni through a single, simple, more flexible, and efficient GN combustion process that is both socially and environmentally viable, by varying the calcination conditions to obtain the desired nanoparticles.

Herein, this work focuses on the synthesis of NiO and Ni nanoparticles via a facile and environmentally benign NCC-assisted GN combustion technique. The physicochemical properties of the as-prepared NiO and Ni were characterised using X-ray diffraction (XRD), Raman spectroscopy, thermogravimetric analysis (TGA), and Fourier transform infrared spectroscopy (FTIR). Field emission scanning electron microscope (FE-SEM) and transmission electron microscope (TEM) were also used to analyse the morphology of the prepared NiO and Ni nanoparticles. The synthesised NiO nanoparticles may be applied as nanocatalysts to suppress tar formation during biomass pyrolysis. These nanoparticles may also be used as nanocatalysts in biomass gasification to increase the hydrogen yield and efficiency of heavy tar removal.

2. Experimental

2.1. Materials

Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$) of 99.5% purity was purchased from Merck KGaA, while glycine ($C_2H_5NO_2$) with a purity of ≥ 99% was supplied by Sigma-Aldrich. NCC (supplied by the University of Maine) was used as the template in the glycine-nitrate combustion synthesis of nano-Ni and nano-NiO particles. All chemicals were of analytical grade and were used without any further purification.

2.2. Synthesis of NiO and Ni nanoparticles

The precursor was first prepared by making NCC and nickel nitrate stock solution. NCC was dispersed in deionized water to prepare a 2 wt % mixture. Nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$) was dissolved in deionized water to obtain a composition of 10 wt% nickel nitrate solution as an oxidizer in the combustion synthesis. Both solutions were stirred and then, the nickel nitrate solution was poured into the NCC dispersion. The mixture was thoroughly mixed using an ultrasonic mixer at 40% amplitude for 3 min, with 5 s pulse on and 5 s pulse off to ensure that the NCC was completely dispersed. Then, the ultrasonicated mixture was subjected to 24 h of continuous stirring on a magnetic stirrer to allow adequate contact time between the nickel ions and NCC. After the homogeneous mixing was completed, a molar ratio of 1.25 of glycine fuel to the total nickel cations was added, and the mixture was stirred for another 5 min. The mixture or the precursor was then transferred into a crucible and dried at 50 °C in an oven. The dried precursor was then calcined in a furnace at different calcination temperatures and duration, with a ramping rate of 5 °C/min to obtain the final NiO/Ni product. In this study, calcination temperature was ranged between 400 and 600 °C, while the calcination time was ranged between 2 and 6 h. After the furnace was cooled down to room temperature, the calcined product was collected and ground using a pestle and mortar to form NiO/Ni powders for further analysis and for evaluating the proposed method of synthesising nanoparticles.

2.3. Characterization

2.3.1. Field emission scanning electron microscope (FESEM)

The morphology and size of the as-synthesised nanoparticles were examined using a field emission scanning electron microscope (FESEM) (Hitachi SU8010, Japan). Each specimen was pressed onto conducting carbon tape, which was applied on a 15 mm sample holder. Then, the specimen was dried in the oven for an hour. The dried specimen was then coated with gold particles using a sputtering machine prior to being viewed under FESEM.

2.3.2. Transmission electron microscope (TEM)

The morphology of the synthesised nanoparticles was further examined using high-resolution transmission electron microscopy. Each specimen was dispersed in ethanol and a few drops of the sol were loaded onto the TEM stage. The specimen on the specimen stage was left to dry in an oven before viewing under the microscope. TEM images were obtained on a FEI Tecnai G220 S-Twin HRTEM (The Netherlands), with an electron kinetic energy of 200 kV.

2.3.3. Thermogravimetric analyser (TGA)

The thermal decomposition behaviour of the precursor (15 mg) was studied using a thermogravimetric analyser (TGA Q500, USA) operated in air atmosphere at a flow rate of 40 mL/s. A temperature calibration for TGA/DTA analysis was conducted and monitored during a thermal process, starting from ambient temperature to 800 °C at a heating rate of 5 °C/min.

2.3.4. X-Ray Diffraction (XRD)

The crystalline structure of the synthesised powder was determined using X-ray diffraction (XRD) analysis and confirmed with Raman spectroscopy. XRD analysis was conducted using a Bruker D8 Advance (USA), with nickel-filtered Cu K α radiation of $\lambda = 0.1541$ nm, at a rate of $0.0564^\circ\ s^{-1}$, and operating conditions of 40 kV and 40 mA. The XRD patterns were collected at room temperature with a step scan of $30^\circ \leq \theta \leq 90^\circ$. The average size of the nanocrystallites can be estimated using Scherrer equation [41–43].

2.3.5. Raman spectroscopy

The synthesised nanoparticles were also analysed using a Renishaw