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Effective reduction in the nanoparticle sizes of NiO obtained via the pyrolysis of nickel malonate precursor modified using oleylamine surfactant

Roussin Lontio Fomekong [a,b,*], John Ngolui Lambi [a], Guy Roland Ebede [a], Patrice Kenfack Tsobnang [c], Hypolite Mathias Tedjieukeng Kamta [a], Cedrik Ngnintedem Yonti [a], Arnaud Delcorte [b]

[a] *Chemistry Department, Higher Teacher Training College, University of Yaoundé I, B.P. 47, Yaoundé, Cameroon*
[b] *Institut de la Matière Condensée et des Nanosciences, Université Catholique de Louvain, Croix du Sud 1, 1348 Louvain-La-Neuve, Belgium*
[c] *Chemistry Department, University of Dschang, PO Box 96, Dschang, Cameroon*

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ABSTRACT

Nickel oxide nanoparticles were synthesized via thermal decomposition of two precursors, the first, a simple nickel malonate and the second, a nickel malonate modified by oleylamine, a surfactant, both having been synthesized by precipitation. While FTIR, TGA and ToF-SIMS were used to characterize the two precursors and to show the presence of oleylamine in the modified precursor, XRD, SEM, TEM and BET were employed to investigate the structure, the morphology and the specific surface area of the decomposition products obtained after pyrolysis. The results showed that the modification of nickel malonate by oleylamine was effective. The XRD results, which showed a cubic structure for the NiO obtained, suggest with SEM an important particle size reduction (at least 54%) when oleylamine was used to modify the nickel malonate precursor. The SEM images also showed a well-defined spherical nanoparticle morphology in both cases, not affected by the presence of oleylamine. The TEM also confirmed the reduction of particle size and their spherical nature but at the same time showed that, in the presence of oleylamine, there was no agglomeration resulting in a more uniform particle size distribution. The specific surface area of the NiO obtained by the oleylamine-modified precursor was 4.7 times larger than that obtained with the regular precursor. This again confirms the particle size reduction.

1. Introduction

Nanoscale materials display physical and chemical properties that are different from those of their bulk counterparts [1]. This difference can be attributed to surface effects (causing smooth properties scaling as a function of the fraction of atoms at the surface) and to quantum effects (showing discontinuous behavior due to quantum confinement effects in materials with delocalized electrons) [1]. In fact the particle size influences the physical phenomena occurring in the material (electron and heat transfer, for example). For instance, the surface area of a material increases with decreasing particle size, and this affects directly many properties such as catalysis and gas sensing [2,3]. As a result, a new range of technological applications of nanomaterials has been developed in the last decade. For these reasons, design and optimization of synthetic methods for the production of nanoparticles have been intensively investigated and important progress has been made in the synthesis of nanomaterials with tailored composition, size, shape, and crystalline structure. However, there is still a strong need for the development of simple and inexpensive protocols for large-scale synthesis of high quality nanoparticles.

Nickel oxide (NiO) nanoparticles have particularly attracted the attention of scientists because of their very interesting characteristics such as good chemical stability, good optical, magnetic and electrical properties, and the fact that they are frequently used as a model for p-type metal oxide materials [4–6]. The electronic properties of NiO have specifically driven research interests in applications such as anodes for lithium ion batteries [7], solar cells [8], electrochromic coatings [9], composite anodes for fuel cells [10], antiferromagnetic materials [11] and gas sensors [12,13]. Regarding its synthesis, several methods have been reported in the literature, notably, solvo/hydrothermal reaction [14], sol–gel process [15], microwave synthesis [16], solution–combustion [17] and

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* Corresponding author.
E-mail addresses: lonforou@yahoo.fr, roussin.lontio@uclouvain.be, roussin.lontio@gmail.com (R.o.s. Lontio Fomekong).

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precipitation followed by thermal decomposition [18]. In particular, the latter is simple, low cost, well controlled and readily yields high purity products. With this method, it is possible to add one or more surfactants to influence the final particle size. In fact, it has been demonstrated that a surfactant has a great influence on the particle size of the material [19].

Oleylamine (OAm) is a long-chain primary alkylamine surfactant which, just like octadecylamine (ODA) or hexadecylamine (HDA), can act as an electron donor at high temperatures. Interestingly, commercial OAm has a much lower cost than commonly used pure alkylamines, though some concerns regarding purity and reproducibility have also been raised [19]. Moreover, the fact that OAm is liquid at room temperature, may facilitate the washing procedures that follow the chemical synthesis of nanoparticles. However, care should be taken in handling OAm since, as indicated in the material safety data sheet, it can be corrosive to the skin [19].

While a search in the literature shows that the thermal decomposition of many metal malonates [20,21] and in particular nickel malonate [22,23], have been investigated, the latter study addressed the synthesis of NiO nanoparticles from such a precursor and the influence of the surfactants on this synthesis seems to be scarce [24]. We, thus, provide in this article, ample evidence that oleylamine is an effective surfactant for the size reduction of the of NiO nanoparticles obtained via the pyrolysis of nickel malonate pre-synthesized by precipitation.

2. Experimental section

2.1. NiO synthesis

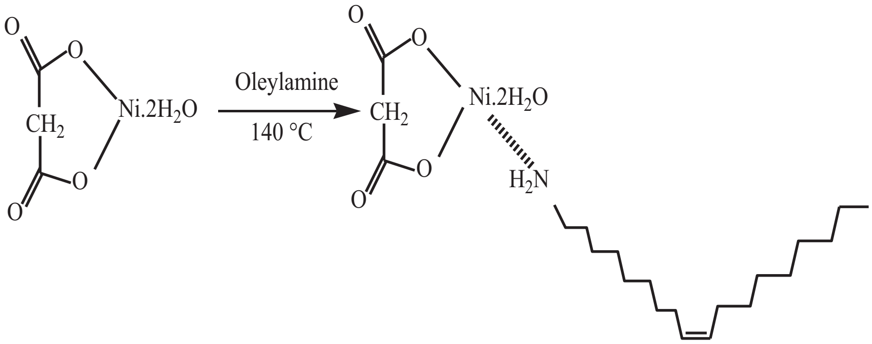
Hydrated nickel chloride ($NiCl_2 \cdot H_2O$), hydrated lithium hydroxide ($LiOH \cdot H_2O$), malonic acid ($HOOCCH_2COOH$) and the surfactant, oleylamine ($CH_3(CH_2)_7CH{=}CH(CH_2)_8NH_2$), all obtained from Aldrich, ethanol and acetone obtained from MERK were used without further purification.

NiO nanoparticles were obtained via two experimental steps: the synthesis of the precursor and its subsequent decomposition. Two syntheses were carried out for the precursor. In the first synthesis (without any surfactant), the precursor, nickel malonate ($NiCH_2C_2O_40 \cdot 2H_2O$), code-named NiM, was prepared according to the procedure described in the literature [25] and calcined in a ceramic combustion boat holder at 500 °C in a muffle oven at a heating rate of 10 °C/min for 1 h under air flow. In the second synthesis (with the surfactant), 1.2 g of the previously synthesized nickel malonate were placed in a round bottom flask, 10 mL of oleylamine added and the mixture heated, with continuous stirring, in an oil bath for 1 h at 140 °C. The resulting light green solution was cooled to room temperature and an excess of ethanol added. The green precipitate obtained after filtration was washed several times with ethanol and dried at 100 °C for 4 h (Scheme 1). The precursor, modified by the surfactant and code-named NiMO, was calcined in a ceramic combustion boat holder at 500 °C in a muffle oven at a heating rate 10 °C/min for 1 h under air flow.

2.2. Characterization methods

The two synthetized precursors were characterized by FTIR and TGA, and the decomposition products by XRD, SEM, TEM and BET.

The functional groups of the malonate ligand and the oleylamine were elucidated using Fourier Transform Infra-Red (FTIR) spectroscopy on the QuickLock Single Reflection Horizontal ATR Accessory from Bruker. The Thermal behavior of the precursor was studied by Thermogravimetry Analysis (TGA) on a METTLER TOLEDO Thermal Analyzer in air and in nitrogen at a flow rate of 100 mL min^{-1}, in the temperature range 25–900 °C and at a heating rate of 10 °C min^{-1}. The presence of oleylamine in the NiMO precursor was confirmed using Time of Flight Secondary Ions Mass Spectrometry (ToF-SIMS) on an IONTOF V spectrometer (IONTOF GmbH, Munster, Germany). The samples were initially bombarded with Bi_5^+ ions (30 keV, 45°) and the resulting secondary ions accelerated at 2 kV before entering the analyzer and post-accelerated at 10 kV before detection. The surface area of analysis was 200×200 μm^2, the data acquisition time was 2 min and the primary ion dose was 4.12×10^7 ions cm^{-2}. The Powder X-ray Diffraction (PXRD) data for the decomposition products were collected at room temperature with a D5000 Siemens Kristalloflex $\theta-2\theta$ Powder Diffractometer. This diffractometer had a Bragg-Brentano geometry and was equipped with a graphite-monochromated Cu-Kα ($\lambda = 1.54056$ Å) radiation, a standard scintillation counter detector and an automatic sample changer which could accommodate 30 samples. For the experiment, the decomposition products were spread out on a flat silicon plate in such a manner as to avoid preferred orientations. The patterns were recorded in the range of 5–90° with a scan step of 0.02° (2θ) and a 2 s step^{-1} acquisition interval. These patterns were compared to the NiO pattern of the ICCD using HighScore Plus Software for phase identification. The recorded patterns were also indexed and the unit cell refined by using the FullProf-suite program [26]. The morphology of the decomposition products was determined by Scanning Electron Microscopy (SEM) using a high resolution FEG JEOL7600F with an accelerating voltage of 15 kV. The images were obtained with the semi-in-lens secondary electron detector. The particle sizes were also estimated by SEM. The morphologies of the samples were confirmed by transition electron microscopy (TEM, Leo922 Model from Zeiss) with an accelerating voltage of 120 kV. TEM samples were prepared by dropping a sonicated water dispersion suspension of the powder samples on a carbon-coated copper grid. Textural analyses were carried out on Micromeritics Tristar 3000 equipment using N_2 adsorption/desorption at 77.150 K. Samples were degassed under



Scheme 1. Illustration of the reaction between nickel malonate and oleylamine.