Nanopowder synthesis of nickel oxide via solochemical processing: effect of dissolution temperature on structure and morphology

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Abstract

NiO nanopowder was synthesized via solochemical method using a nickel containing complex solution. This was a simple economic way leading to 13 nm particles characterized by XRD, SEM, TEM and BET tests. Micrographs revealed that the particles had elongated particulate shape with a narrow size distribution. Solochemical processing can thus be an attractive method for industrial production of the nanopowders.

Keywords: NiO; Nanoflake; Nanowall; Solochemical; TSSC

Introduction

Nanostructured materials have extensively been explored for fundamental scientific and technological interests to access new classes of functional materials with unprecedented properties and noteworthy applications [1]. Nickel oxide has a wide range of applications in the manufacture of ceramic composite parts, magnetic materials, alkaline battery cathodes, anti ferromagnetic layers, p-type transparent conducting films, electrochromic films, heterogeneous catalytic materials and gas sensors [2-8]. Numerous routes like ultrasonic radiation, hydrothermal synthesis, carbonyl method, laser chemical processing, microwave pyrolysis, sol–gel technique, precipitation-calcination, microemulsion scheme and mechanochemical processing have previously been investigated for production of NiO nanopowders [9-17].

The reported techniques are mostly limited to the laboratory scale because of specific conditions required, tedious procedure, complex apparatus, low-yield, high-cost and so on. From practical point of view, it is essential to develop an approach to manufacture high-quality nanopowder with large output and low cost. Traditional methods are not economically feasible for mass scale production of nanopowders. Solochemical processing utilized in this research is a two-stage deposition method consisting of a nickel containing complex production and decomposition to end-up with the nickel oxide nanopowder similar to that used for ZnO production during a previous research [18]. Pouring of a limpid chemical onto a second chemical leads to the formation of the desired nanoscale powder.

The solochemically formed nanopowder can further be doped with other oxides to form nanocomposite particles usable in varistores. Results of the most recent studies carried out in our laboratory on synthesis of NiO nanopowder via two-stage solochemical (TSSC) method are reported in this article.

Experimental procedure

Anhydrous $NiCl_2$ powder (Merk, 99.5%) was dried at 150˚C overnight under air and then milled in a simple ceramic mortar. Ammonia was slowly added to the powder while vigorously mixed and stirred at 550-700 rpm for approximately 30-60 min to produce $(NH_4)_2NiO_2$ used as Ni^{+2} containing solution. Stirring of the solution continued for 20–30 min and distilled water was added until green precipice appeared. The procedure was repeated at 20, 33, 55 and 75°C. Chemical reactions ending up with the NiO nanopowder can be written as follows:

$$NiCl_2(s)+2NH_4OH(l) \rightarrow (NH_4)_2NiO_2(l)+2HCl(l)$$
$$(NH_4)_2NiO_2(l)+H_2O(l) \rightarrow NiO(s) + 2NH_4OH(l)$$

Addition of NH_4OH resulted in dissolving of the precipitate while distilled water addition helped stabilization of the precipitate. The precipitate was filtered, twice washed with distilled water and then with ethanol. It was subsequently dried at 105°C for 90 min and heated at 410°C for 1 hr.

The NiO powder was analyzed with x-ray fluorescence (XRF) and characterized by x-ray diffraction (XRD) Cu K_α radiation, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Brunauer-Emmett-Teller analyzer (BET).

Results

X-ray fluorescence

XRF analyses indicated that the NiO content of the calcined powder was 99.8%. This meant that the solochemical process had resulted in NiO formation according to the second reaction.

X-ray diffraction

Fig. 1 depicts x-ray diffraction spectrum of the nanopowder samples produced by SC method in various solution temperatures: (a) the dried precipitate and (b) the calcined product. The dried precipitate shown in Fig. 1(a) do not show significantly sharp peaks. This indicates that the precipitate is amorphous. When calcined at 410°C, rhombohedral NiO crystals would appear. The diffraction peaks of the calcined NiO precipitate indicate small particle sizes averaged by Scherrer formula to be 13 nm:

$$D = 0.9\ \lambda/B\ (\cos\theta)$$

According to the Fig. 1 (right side patterns), the effect of the solution temperature is a slight decrease in the XRD count number indicating slightly less NiO formation.

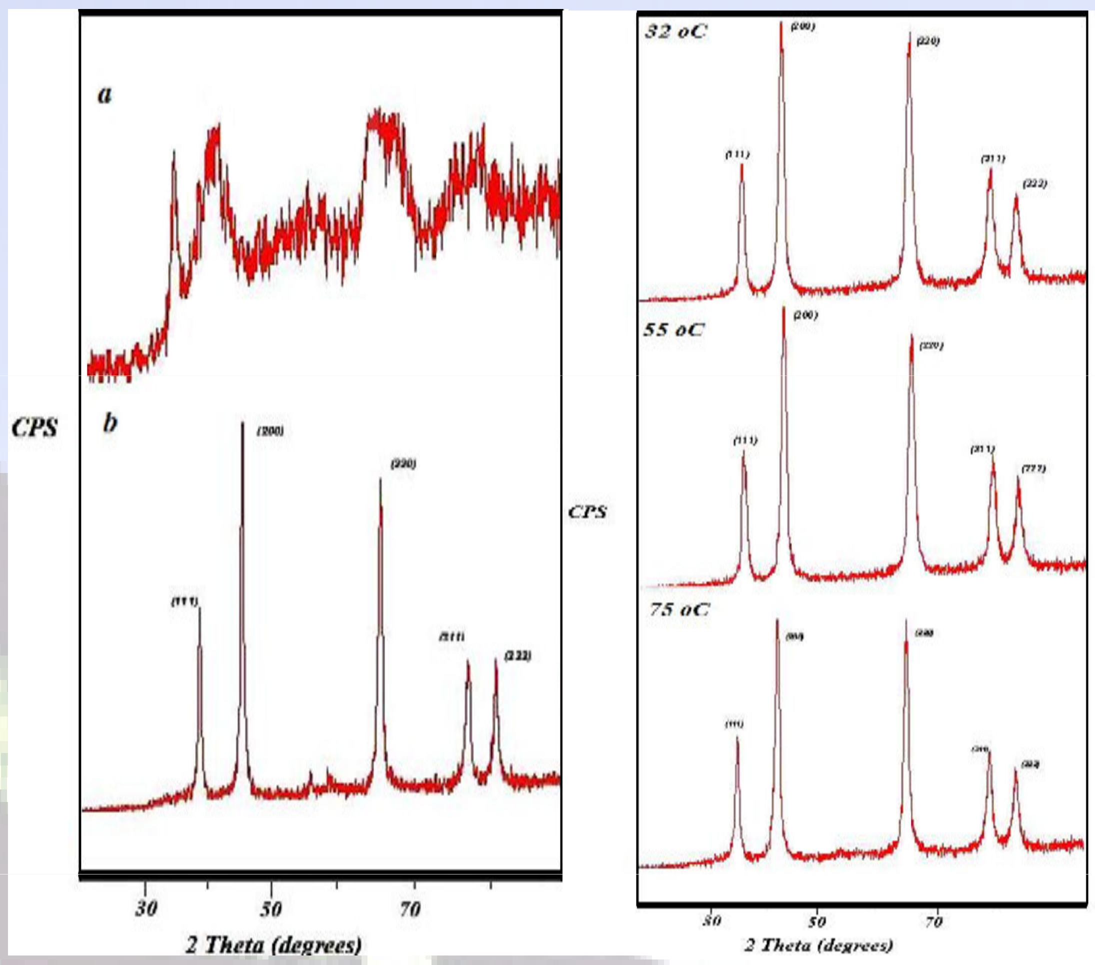

Fig 1. X-ray diffraction spectrum of the nanopowder sample produced by TSSC method: (a) as dried precipitates and (b) precipitate after calcination. The patterns on the right-side indicate the effect of temperature on the calcined product.

Scanning Electron Microscopy (SEM)

Fig. 2 indicates the SEM micrographs of the NiO nanopowders produced by TSSC method at different temperatures. Wall-shaped flakes appeared at lower temperatures (i.e. 20˚C). Their shape significantly changed towards sharp-wall grains with increasing of the temperature. It seems that the TSSC nature significantly affects the morphologies of the nanopowder. Fig. 2(a) indicates that flake-shaped grains prevail when TSSC occurs at 20˚C. Flake proportion reduces, however, by TSSC processing temperature. At 55 and 75ºC, the particles grow into sharp walls observable in Fig. 2(c and d). Walls are highlighted by barbs in this figure. Partial agglomeration also occurs at these higher processing temperatures (T=55 and 75ºC).

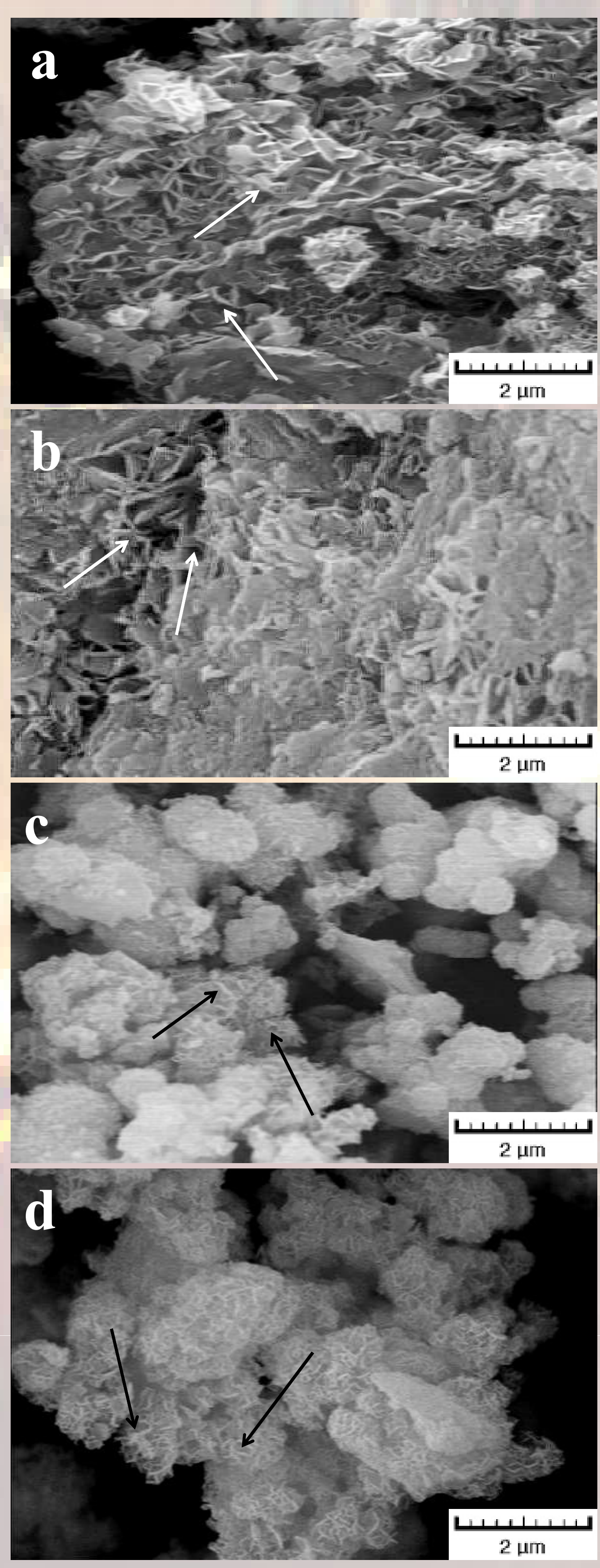

Fig 2. SEM micrograph of the NiO powder synthesized by the TSSC at: (a) 22, (b) 32, (c) 55, (d) 75 degrees Celsius. The arrows highlight wall-shaped NiO nanoparticles.

Transmission Electron Microscopy (TEM)

A typical TEM micrograph of the TSSC NiO powder processed at the room temperature is demonstrated in Fig. 3. The powder consists of nanoparticles having ~20 nm diameter with wall-shaped flakes. TEM morphology indicates separate nanoparticles produced by the TSSC processing of the aqueous solution. Fig. 4 shows the diffraction pattern (DP) imaging of the produced nanopowder. Sharp diffraction rings with strong diffraction spots appear in the pattern. The diffraction pattern corresponds with the nickel oxide particles without any amorphous phase. Dark field imaging revealed that each particle was a single crystal. Due to the difference between the temperatures of the two chemical solutions, the formation of NiO nanopowder was accompanied with a thermal shock which resulted in production and increasing of porosity of the powders, especially within the enlarged particles that sensed greater shock effects. The nanowalls produced in this research can be used in gas sensors devised for air pollutants detection. These nanowalls incorporate innovative specifications obtained for the first time. The BET surface area of the NiO powder produced at the solution temperature 75˚C is ~80 m²/g; a large surface area boding the porous microstructure of the wall-shaped NiO nanoparticles.

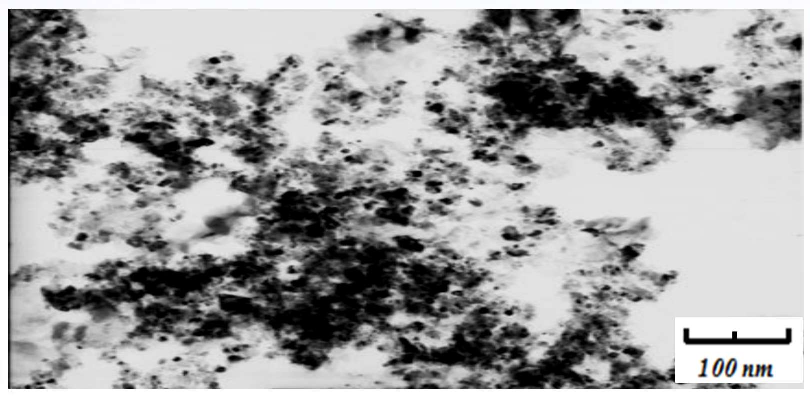

Fig 3. TEM micrograph of the NiO nanopowder produced by the TSSC method at the room temperature.

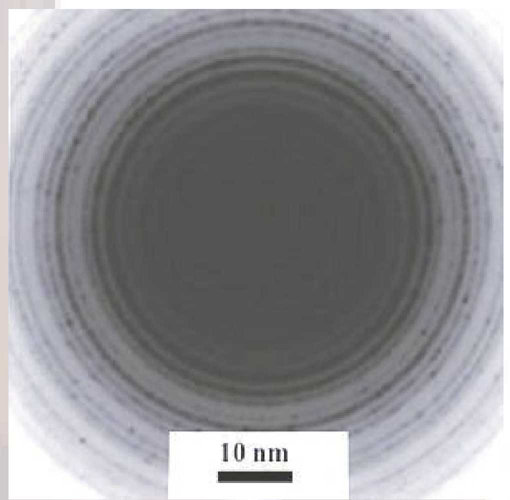

Fig 4. Diffraction pattern image of the produced nanopowder.

Conclusion

High quality NiO nanopowder can easily be synthesized by solochemial treatment of an aqueous nickel containing solution. NH_4OH and anhydrous $NiCl_2$ are the row materials with H_2O functioning as the solvent. Depending on the amount of temperature, the product consists of a proportionate amount of both nanowalls and nanoflakes. Solution temperatures as high as 75˚C can lead to the formation of sharp-wall nanograins with specific surface area of ~80 m²/g. High purity NiO made by the TSSC process seems most suitable for such applications as gas sensors, heterogeneous catalysis and alkaline battery manufacture.

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