Long-Chain Alkyl Surfactant Assisted Preparation of Nano-Nickel Oxide via Hydrothermal Synthesis Method

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Abstract. The nano-NiO was prepared by hydrothermal synthesis method, using nickel sulfate hexahydrate as raw materials, urea as precipitant, and long chain alkyl ionic liquid 1-hexadecyl-3-methyl-midazolium chloride as surfactant, respectively. X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), and other analytical methods were used to characterize the particle size, the phase and microstructure, and morphology of the prepared samples. Thermal stability of the samples was studied by thermogravimetry (TG). The molecular structure of nickel oxide was analysed by making use of the Fourier transform infrared spectroscopy (FT-IR). The results show that all the precursors synthesized via hydrothermal synthesis method were converted into NiO after sintering, and the obtained nano-NiO particles have good dispersibility and regular morphology, simultaneously possessing uniform size, and high purity. The samples prepared are belong to cubic structures with an average particle size of about 5-20 nm.

Keywords: Nickel Oxide, Hydrothermal Synthesis, Long-Chain Alkyl Surfactant

1 Introduction

Transition metal oxide NiO is a P-type semiconductor material, which the theoretical specific capacitance is high, the cycle stability is good, the price is low, the source is extensive, and is the environment-friendly supercapacitor. At present, NiO is widely used in field of lithium ion batteries, supercapacitors, biosensors, gas sensors, electrochromic films, and catalysis because of having excellent properties, such as electrical properties and chemical stability [1-4]. Therefore, the research on the synthesis and application of nano-nickel oxide has been highly valued.

The synthesis methods of NiO nanomaterials are mainly adopted currently as follows [5-9], such as hydrothermal/solvothermal method, chemical precipitation method, sol-gel method, electrochemical deposition method, microwave-assisted synthesis and other methods. The most common current method for synthesizing nano-nickel oxide is the hydrothermal synthesis method, but the problem of easy agglomeration between nano-nickel oxide particles is difficult to solve during the preparation procedure. Therefore, under the premise of ensuring the performance of nano-nickel oxide, the nano-sized nickel oxide with good size and shape can be produced, and expand its application field by
changing the process. The preparation and application of nano-nickel oxide have become a hot topic in the field of materials science. Especially, the preparation of hetero-phase-free high-purity nano NiO has become a research hotspot in this field. In order to solve the problem of easy agglomeration between nickel particles in the hydrothermal synthesis process, a common method is to introduce a surfactant during the preparation process; the purpose is to reduce the agglomeration problem between the nanoparticles. Common surfactants such as sodium dodecyl benzene sulfonate, polyethylene glycol, polyvinylpyrrolidone (PVP) are adopted [10], but there are few reports on the use of ionic liquids as surfactants to assist with synthesis of the nano-NiO in the preparation of nickel oxide nanoparticles, especially long-chain alkyl surfactants, the work on the preparation of nickel oxide nanoparticles is worthy of study by using ionic liquids as surfactants.

Nanomaterials prepared by hydrothermal synthetic methods have outstanding characteristics such as high purity, uniform size, controllable morphology, and large specific surface area. Herein, the nano-NiO was prepared by adopting a mild and simple hydrothermal synthesis method, using water as a solvent, urea as a precipitant, and 1-chloro-hexadecane-3-methylimidazole as a surfactant, and the crystal structure and microstructure of the samples are studied in this work.

2 Experimental

2.1. Reagents and instruments
Nickel sulfate (NiSO₄·6H₂O), urea (CO(NH₂)₂), sodium lauryl sulfate (SDS), 1-chloro-hexadecane-3-methylimidazole (C₁₆mimCl) All are analytical reagents, JJ-1 timing electric mixer, muffle furnace, vacuum pump, etc.

2.2. Synthesis of samples
The nanoparticles of NiO were synthesized by using hydrothermal synthesis procedure. C₁₆mimCl was prepared according to the references [11]. According to the stoichiometric proportions relationship, the appropriate amount of metal salts (NiSO₄·6H₂O), Surfactant (C₁₆mimCl) and urea (CO(NH₂)₂) are weighed and dissolved in distilled water, respectively. On the other hand, the C₁₆mimCl was dissolved at room temperature until its complete dissolution was assured. Then, add a certain amount of urea (CO(NH₂)₂), the dissolved nickel sulfate (NiSO₄·6H₂O) was added to the prepared solutions successively, and stirred magnetically, reacted for one hour. Then, transferred the mixture to the inner Teflon stainless steel autoclave sealed and crystallized at 80°C for 72 h. The reaction was completely cooled to room temperature to obtain a green precipitate, which was filtered with suction, washed repeatedly with deionized water and absolute ethanol, and dried under vacuum at 60°C for 24 h. The obtained powder was calcined in a muffle furnace at 350°C for 3h to obtain a NiO black powder. At the same time, samples without surfactant and sodium dodecyl sulfate surfactant were also prepared; the method is the same as above.

2.3. Characterization of samples
The crystal structure of the sample was analyzed and tested by using the Japanese science TTR III type target X-ray diffractometer. The test conditions were: Cu target, KA wire, tube voltage 40 kV, tube current 200 mA, and scanning speed 10°/min. Field emission scanning electron microscope (FESEM) (NOVA NANOSEM-450) from American FEI company and JEM-2100F field emission transmission electron microscope (TEM) from Japanese electronics company were used to observe the surface morphology of the samples. The thermo-gravimetric analysis of the thermal decomposition behavior of NiO precursors was performed on a German NETZSCH STA449F3 integrated thermal analyzer. Infrared spectroscopy was performed on a PE type Frontier in the United States to analyze the molecular structure of the samples.

3 Results and discussion
3.1. XRD analysis of samples

![XRD Image of nano-NiO after calcination](image)

**Fig. 1** XRD image of nano-NiO after calcination

The XRD patterns of NiO samples were obtained by sintering nickel oxide precursors prepared using C16mimCl as a surfactant. The map is shown in Figure 1. It can be seen from Figure 1 that the diffraction peaks of nickel oxide at 2θ angles of 37.46°, 43.28° and 62.92°, which can be indexed to (111), (200) and (220) crystal plane, respectively, the diffraction peaks of nickel oxide at 2θ angles of 75.44° and 79.50° are very weak. The peak positions and intensities completely are in good agreement through comparison to the NiO standard spectrum (JCPDS NO.71-1179), the sharp peaks indicate that NiO was in the present sample. It is found that the prepared nickel oxide has similar diffraction peak to that of NiO. The presence of Ni impurity peaks was not observed in the XRD patterns of the calcined NiO powders at 350°C, which indicated that NiO precursor obtained from the hydrothermal reaction may be Ni(HCO$_3$)$_2$, and all the precursors were converted into NiO after sintering. The above results show that high purity NiO powder was synthesized under hydrothermal synthesis conditions, which belongs to cubic crystal structure. The XRD diffraction peaks of NiO nano-particles broadened obviously and the peak shape intensity was larger, which means that the particles formed are smaller and the crystallization of NiO nano-particles is complete, which shows that the crystallization effect is better. This high-purity NiO crystal powder is expected to become a lithium ion battery anode material with good electrochemical performance. The average particle size of nickel oxide is about 23 nm by the estimation of the Scherrer formula (D=Kλ/βcosθ).

3.2. SEM analysis of samples

The morphology of NiO was studied by field emission Scanning electron microscope (SEM). Figure 2 is the SEM image of the prepared NiO sample. It can be seen from the figure that the nickel oxide prepared by adding an ionic liquid surfactant takes on a wide variety of shapes, such as regular polyhedron, hexagonal prism and cube, the morphology of the particles is obviously different, which is further confirmed from the scanning electron microscopy image. The diameter of nano-sized nickel oxide particles is varying simultaneously.
3.3. TEM analysis of samples
The microstructure of the NiO was investigated using TEM, the TEM images of nano-nickel oxide particles obtained by adding different surfactants are shown in Figure 3. It can be seen from Figure 3(a) that the samples without adding surfactants have serious agglomeration and larger particle sizes. Figure 3(b) is the TEM image of the NiO samples with adding SDS surfactant. The agglomeration of the sample with SDS surfactant is less serious than that without the surfactant, and some particles are NiO clearly visible. From Figure 3(b), it can be seen that the NiO sample obtained after high temperature treatment has a plate-like shape appearance, the diameter is about 10-20nm, there is some agglomeration between the particles. The TEM images of nano-nickel oxide particles obtained by adding ionic liquid C_{16}mimCl surfactants are shown in Figure 3(c). The nano-NiO particles obtained after high temperature treatment have cubic and square in shape, and were slightly agglomerated, which possess good dispersibility and uniform particle size distribution. The above experimental results show that the addition of ionic liquid C_{16}mimCl has a certain effect on the synthesis of nanoparticles, it is not easy to agglomerate between nanoparticles, and the size of the synthesized particles is uniform. The particle size was in the range of 5-20 nm, which was consistent with the average crystallite size calculated from the XRD pattern.
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(c) C_{16}mimCl surfactant

**Fig. 3** TEM image of nano-NiO by adding different surfactant after calcination

3.4. *FT-IR analysis of samples*

As shown in Fig. 4, the molecular structure and chemical bond properties of the samples were investigated by infrared spectrum analysis. The number and location of absorption peaks are attributed to the chemical composition, crystalline properties, and morphology of the material. The absorption band below 1000cm\(^{-1}\) is considered as a necessary condition to study the existence of metal-oxygen bonds in the samples. [12]. In FT-IR spectra, the sharp vibration peaks at 3432, 1625, 1112cm\(^{-1}\) are attributed to water molecules and the weak broad peak at 462cm\(^{-1}\) is assigned to Ni-O bond stretching vibration [13]. The results are consistent with that of XRD; the nickel oxide sample is of high purity.

![FT-IR image](image)

**Fig. 4** FT-IR image of nano-NiO after after calcination

3.5. *TG analysis of precursor thermal decomposition behavior*

The thermal stability of the samples was investigated by the thermogravimetric analysis (TG), and also the quality change of the samples in nitrogen atmosphere was observed. In order to understand the thermal decomposition behavior of the sample during sintering, thermogravimetric analysis was carried out from 30 to 1200\(^\circ\)C at a heating rate of 20\(^\circ\)C/min under oxygen atmosphere. The results are shown in Figure 5. Figure 5 shows the TG curve of NiO precursor samples in air atmosphere. It can be seen from the figure that the sample is mainly divided into three stages: the first stage is 25-130\(^\circ\)C, which corresponds to the loss of absorbed water and crystal water in the sample, the weight loss is about 15%; the second stage is 130\(\sim\)400\(^\circ\)C, the weight loss is faster than the first stage (the weight loss is about 28.7%), mainly because the organic complex gradually begins to decompose at this stage; the third stage is 400 to 800\(^\circ\)C, the weight loss is faster (the weight loss is about 63.3%); when the temperature is higher than 850\(^\circ\)C, the sample mass no longer changes, indicating that the nickel oxide precursor is almost completely decomposed at 800\(^\circ\)C, and the precursor sample has been completely converted into NiO. This shows that the synthesized nickel oxide has good thermal stability.
Fig. 5 TG curve of NiO precursor at heating rate of 20°C/ min

4 Conclusion

Cubic nano-NiO was synthesized by hydrothermal method using nickel sulfate hexahydrate as main raw material, urea as homogeneous precipitant and ionic liquid as Surfactant. The properties of the precursor and the samples were characterized by TG, XRD and TEM. The results show that the precursor completely decomposes to NiO before 800°C and has good thermal stability. Ionic liquids C16mimCl can promote and assist the synthesis of nano-NiO to some extent. The obtained nano-NiO is belonging to cubic crystal structure, possessing uniform particle size and good dispersibility. The average particle size is about 5-20m.

Acknowledgements

This research has been supported by the Youth Project for Applied Basic Research in Yunnan Province (Project No.: 2012FD065), the Scientific Research Fund Project of Yunnan Provincial Department of Education (Project Number: 2012YS04 and 2011Y425), and supported by the research team of Yunnan Open University (Hybrid Functional Materials Research Team)

References

[1] Zhao Yongjie, Zhang Xiaowei, Xu Xiangming, et al: Synthesis of NiO nanostructures and their catalytic activity in the thermal decomposition of ammonium perchlorate. CrystEngComm, 18, 4836-4843 (2016).
[2] K. Zrikem, G. Song, A. Ait Aghzzaa, et al: UV treatment for enhanced electrochromic properties of spin coated NiO thin films. Superlattices and Microstructures, 127, 35-42 (2019).
[3] Y. E. Firat, A. Peksoz: Efficiency enhancement of electrochromic performance in NiO thin film via Cu doping for energy-saving potential. Electrochimica Acta, 295, 645-654 (2019).
[4] Zhang Weina, Zhang Xuezhen, Wu Tongyue, et al: Interface engineering with NiO nanocrystals for highly efficient and stable planar perovskite solar cells. Electrochimica Acta, 293, 211-219 (2019).
[5] M. Naseem Siddique, Ateeq Ahmed, P. Tripathi: Electric transport and enhanced dielectric permittivity in pure and Al doped NiO nanostructures. Journal of Alloys and Compounds, 735, 516-529 (2018).
[6] Xu Ju, Wang Meiri, Liu Yuanyuan, et al: One-pot solvothermal synthesis of size-controlled NiO nanoparticles. Advanced Powder Technology, 30(4), 861-868 (2019).
[7] Julien Keraudy, Axe lFerrec, Mireille Richard-Plouet, et al: Nitrogen doping on NiO by reactive magnetron sputtering: a new pathway to dynamically tune the optical and electrical properties. Applied Surface Science, 409, 77-84 (2017).
[8] Do Dang Trung, Nguyen Duc Cuong, Pham Long Quang, et al: Facile post-synthesis and gas sensing properties of highly porous NiO microspheres. Sensors and Actuators A: Physical, 296, 110-120 (2019).
[9] K. Varunkumar, Rafikul Hussain, Gurumurthy Hegde, et al.: Effect of calcination temperature on Cu doped NiO nanoparticles prepared via wet-chemical method: structural, optical and morphological studies. Materials Science in Semiconductor Processing, 66, 149-156 (2017).

[10] S. Zargouni, L. Derbali, M. Ouadhour, et al.: Elaboration and characterization of PVP-assisted NiO thin films for enhanced sensitivity toward H2 and NO2 gases. Ceramics International, 45(5), 5779-5787 (2019).

[11] Liu Longjiang, Wang Tongwen, Liu Ling, et al. Synthesis of Fe-, Co- and Ni-Containing MCM-48 using long-chain ionic liquid template. Chinese Journal of Inorganic Chemistry, 25, 693-699 (2009).

[12] Yang Chengwu, Wöll Christof: IR spectroscopy applied to metal oxide surfaces: adsorbate vibrations and beyond. Advances in Physics, 2(2), 373-408 (2017).

[13] J. Al Boukhari, L. Zeidan, A. Khalaf, et al.: Synthesis, characterization, optical and magnetic properties of pure and Mn, Fe and Zn doped NiO nanoparticles. Chemical Physics, 516, 116-124 (2019).