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A Versatile Route for the Synthesis of Nickel Oxide Nanostructures Without Organics at Low Temperature

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Abstract Nickel oxide nanoparticles and nanoflowers have been synthesized by a soft reaction of nickel powder and water without organics at 100 °C. The mechanism for the formation of nanostructures is briefly described in accordance with decomposition of metal with water giving out hydrogen. The structure, morphology, and the crystalline phase of resulting nanostructures have been characterized by various techniques. Compared with other methods, the present method is simple, fast, economical, template-free, and without organics. In addition, the approach is nontoxic without producing hazardous waste and could be expanded to provide a general and convenient strategy for the synthesis of nanostructures to other functional nanomaterials.

Keywords Nickel powder · Soft synthesis · Nanostructures · Functional materials

Introduction

In recent years, nanomaterials have steadily received growing interests as a result of their peculiar and fascinating properties and applications superior to their bulk counterparts. A wealth of interesting and new phenomena associated with nanostructures has been found with the best established examples including size-dependent excitation and emission. It is generally accepted that the quantum confinement of electrons by the potential well of nanometer-sized structure may provide one of the most powerful means to control the electrical, optical, magnetic, and thermoelectric properties of solid-state functional materials. Thus the ability to generate such minuscule structures is essential to much of modern science and technology [1–4].

Nickel oxide (NiO) has been under extensive investigations for decades as a kind of important functional material. It is regarded as a very prosperous material and can be used as battery cathodes, catalysts, gas sensors, electrochromic films, and in magnetic materials [5–8]. Because of the volume effect, the quantum size effect, and the surface effect, nanocrystalline NiO is expected to possess many improved properties than those of micro-sized NiO particles. The particle structural property (particle size, distribution, and morphology) is closely related to the preparation techniques. So far, various methods on the preparation of NiO nanostructures including nanoparticles and nanoflowers have been reported [9–15]. Wu et al. [9] synthesized NiO nanoparticles of different shapes by four different methods using different amines and surfactants. It was shown that by altering the concentration and composition of solvents, different morphologies having variant diameters, shape, and distribution can be achieved. Tiwari and Rajeev [10] prepared NiO nanoparticles of different sizes by sol–gel method using nickel nitrate as precursor. Microemulsion route has been employed to prepare NiO nanoparticles by using cationic surfactant by Han et al. [11]. Li et al. [12] obtained NiO nanoparticles via thermal decomposition using ethanol as solvent. Wu and Hsieh [13] prepared NiO nanoparticles by a chemical precipitation method. Dharmaraj et al. [14] obtained NiO nanoparticles using nickel acetate as precursor at 723 K. A method for the synthesis of NiO nanocrystals using nickel chloride hydrate as nickel source has been introduced by An et al. [15]. All the above methods for the formation of NiO nanostructures are technically complex,
require high temperature, harsh growth conditions, expensive experimental setup, complicated control processes, and have made frequent use of organics. Seeking a simple approach for low cost, lower temperature, larger-scale production, and controlled growth without additives is desired. The fabrication of nanomaterials emphasis not only size, the geometry, and chemical homogeneity, but also the simplicity and practicability of synthesis techniques. When developing a synthesis method for generation of nanostructures, the most important issue that one needs to consider is the simultaneous control over composition, dimensions, morphology, and monodispersivity. Here in, we report an alternative low temperature approach to the synthesis of NiO nanoparticles and nanoflowers by a soft reaction of nickel powder and water without using organic dispersant or capping agent. To the best of our knowledge, this is the first report of synthesis where water is used as a solvent as well as a source of oxygen. Our studies lay down a convenient producer for the synthesis of NiO nanostructures at low temperature without using organics and templates which may be scaled up for industrial applications. The methodology may provide a one-step, fast, non-toxic, and mass production route for the synthesis of other functional oxide materials.

Experimental

Preparation of NiO Nanostructures

In a typical synthesis, appropriate amount of nickel powder was taken with 20 mL of distilled water in a glass vial and the mixture was well sonicated for about 10 min. The reaction mixture was transferred to teflon-lined stainless steel autoclave of 50 mL capacity before keeping at desired temperature. The autoclave was kept in a furnace, which was preheated to 100°C for different reaction times. After a desired period of time, the autoclave was taken out and cooled to room temperature naturally. The resulting reaction mixture was centrifuged to reclaim the precipitated product. The final product was filtered, washed with deionized water and ethanol several times and finally dried in air.

Structural Characterization

X-ray diffraction patterns of the samples were recorded with Siemens D 5005 diffractometer using Cu Kα (λ = 0.15141 nm) radiation. The morphology and crystalline size of samples were studied by high-resolution field emission scanning electron microscopy (FESEM) (FEI NOVA NANOSEM-600) coupled with energy dispersive spectroscopy. Photoluminescence (PL) spectra were recorded with a Perkin–Elmer model LS55 at room temperature.

Results and Discussions

For the micro-structural analysis, the as-synthesized samples were directly transferred to the FESEM chamber without disturbing the original nature of the products. Figure 1 shows FESEM images of the as-prepared samples obtained by reacting micrometer-sized nickel particles with water under different conditions. Nanoparticles were not observed for a sample reacted for 12 h at room temperature (Fig. 1a), while almost uniform spherical nanoparticles were produced for sample heated at 100°C for 12 h (Fig. 1b). The diameters of the nanoparticles are in the range of 50–70 nm with an average diameter of 60 nm. Using higher reaction time of 24 h, the average diameter of the nanoparticles increased from 60 to 80 nm (Fig. 1c). Our studies indicate that the average diameter of the nanoparticles increases with the increase in reaction time, accompanied by an increase in aspect ratio. A similar study using polyvinylpyrrolidone as precursor has been reported by Tao and Wei [16]. Finally, the reaction mixture was kept for 36 h and nanoflower-like product resulted. Earlier, Yang et al. [17] have reported nickel hydroxide nanostructures including nanosheets and nanoflowers by a hydrothermal methods using NaOH as solvent. This work has ruled out the role played by the solvents and organics in the structural evaluation of NiO nanostructures.

The EDX measurement indicates that nanoparticles are composed of Ni and O, and the analysis in the NiO nanoparticles/nanoflowers indicates an atomic ratio of 86% Ni and 14% O, which is very near to the theoretical value (7% error is attributed to the analysis technique). A typical XRD plot is presented in Fig. 2. The intensity of peaks is well consistent with that of standard JCPDS card No. 04-0835, and the sharp diffraction peak in the pattern can be exactly indexed to cubic structure of NiO with cell constant a = 4.193 Å, which is in agreement as reported in the literature. No characteristic peaks of impurity were observed.

The PL spectrum of nanoparticles and nanoflowers is presented in Fig. 3a, b. The room temperature PL spectra of NiO nanoparticles and nanoflowers show an UV emission band at 325 and 390 nm, respectively. The emission in the UV region is attributed to the recombination between electrons in conduction band and holes in valence band. There is a sharp band in the PL spectra of NiO nanoparticles and nanoflowers at 380 and 490 nm, respectively. The visible emission is related to the defects-related deep level emission such as oxygen vacancies and Ni interstitials. Finally, there are a weak and a broad visible emission band at 600 nm in both the spectra that is usually attributed.
to native defects such as Ni interstitials and O vacancies as suggested by Lyu et al. [18].

The formation of various nanostructures by the reaction of nickel with water can be explained as follows. Nickel gives hydrogen on reaction with water.

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4\text{Ni}(s) + 4\text{H}_2\text{O}(l) \rightarrow 4\text{NiO}(s) + 4\text{H}_2(g).
\]

Here \(s\), \(l\), and \(g\) represent solid, liquid, and gas, respectively. The similar study has been reported earlier, where evolution of hydrogen has been documented by Zhao et al. [19]. The Ni metal on reaction with water slowly gives out hydrogen \((g)\) and the liberated oxygen reacts with metal to give oxides as shown in the above reaction. The Ni reacts with oxygen and forms nuclei, which further serve as seeds for NiO nanostructures growth. The growth of nanostructures could be occurring at the small oxide nuclei that may be present on the metal surfaces. Moreover, water at elevated temperatures plays an essential role in the precursor material transformation because the vapor pressure is much higher and the state of water at elevated temperatures is different from that at room temperature. The solubility and the reactivity of the reactants also change at high pressures and high temperatures, and high pressure is favorable for crystallizations.

Based on the corrosion theory, we know that at high temperature in the absence of oxygen, the corrosion of
nickel by water involves two key component movements: the transport of oxygen-bearing species to the metal/oxide interface and the diffusion of nickel ions become saturated at some points on the surface, a NiO layer then nucleates and grows. The most widely cited classical model for shape control of crystals is given by Gibbs–Curie–Willff theorem. This theory suggests that the shape of a crystal is determined by the surface energy of individual crystallographic faces. The final crystal shape is determined in such a way that the total free energy of the system is minimized. It is believed that the physical and chemical properties of solvent can influence the solubility, reactivity, and diffusion behavior of reagents [20]. In the present reaction, water is only used as a solvent and hence has the same influence on the crystal phases of nanoparticles and nanoflowers.

Conclusion

In summary, NiO nanoparticles and nanoflowers were successfully synthesized by a reaction of nickel powder and water without organics and substrates at 100 °C. This synthetic technique has the following advantages: firstly, it is a one-step synthesis approach, making it easy to control the growth kinetics. Secondly, the synthesis needs no sophisticated equipments since it is conducted at low temperature of 100 °C under normal atmosphere. Thirdly, the clean surfaces of the as-synthesized nanostructures can be readily functionalized for various applications since there is neither a capping reagent nor a substrate. Forth, the approach is non-toxic without producing hazardous waste. Therefore, the technique could be extended and expanded to provide a general simple and convenient strategy for the synthesis of nanostructures of other functional materials with important scientific and technological applications. The relative studies are in process and will be reported in forthcoming publications.

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