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Synthesis of porous nanocrystalline NiO with hexagonal sheet-like morphology by homogeneous precipitation method

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ABSTRACT

Porous nanocrystalline NiO has been synthesized by a simple homogeneous precipitation method in short time at low calcination temperature without using any surfactant, chelating or gelating agents. The porous nanocrystalline NiO with a hexagonal sheet-like morphology were obtained by calcination of $Ni(OH)_2$ nanoflakes at 500 °C. The calcination temperature strongly influences the morphology, crystallite size, specific surface area, pore volume and optical band gap of the samples. The samples were characterized using powder X-ray diffraction, thermal gravimetric analysis, FT-IR spectroscopy, UV–Visible diffuse reflectance spectroscopy, surface area measurements, field emission scanning electron microscopy coupled with energy dispersive X-ray analysis and transmission electron microscopy. The chemical activity of the samples was tested by catalytic reduction of 4-nitrophenol with $NaBH_4$.

1. Introduction

Nano-sized materials have been widely used in different fields because of their unique physical and chemical properties that are completely changed from those of their bulk counterparts. These properties are extensively affected by the morphology, size, shape and crystalline nature of nanomaterials [1–3]. Among transition metal oxides, NiO nanoparticles are important p-type semiconductor with a stable wide band gap (3.6–4.0 eV) [4]. They have potential applications in gas sensors [5], magnetic

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materials [6], solar cells [7], ceramic materials [8] antioxidant [9], supercapacitors [10], anodes for lithium ion batteries [11,12] and catalysis [13] due to their high chemical and thermal stability. They have also been used as adsorbent for the removal of most toxic Cr (VI) from aqueous solutions [14] and malachite green and acid red in pollutants from waste water [15]. In addition NiO nanoparticles exhibit antibacterial activity against *Escherichia coli*, *Bacillus subtilis*, and *Streptococcus aureus* [16,17]. They are too used as good photocatalysts in the degradation of phenol [18].

There are some organic compounds which are very much harmful in oxidized form but advantageous in reduced form. Such is 4-nitrophenol (4-NP) which is toxic in nature. It is widely used in the production of pesticides, insecticides, herbicides, explosives and synthetic dyes. Therefore, 4-NP and its derivatives are common pollutant in waste water that has been the cause of serious environmental problems [19]. Its reduced form 4-aminophenol (4-AP) is a commercially important intermediate in the synthesis of different analgesic and antipyretic drugs such as acetaminophen, acetanilide, paracetamol and phenacetine [20]. It is also used as an anticorrosion-lubricating agent in fuels, photographic developer, corrosion inhibitor in paints, hair-dyeing agent and so on [21]. Hence, the conversion of 4-NP to 4-AP is a necessary task. There are several methods available for this conversion [20,22,23]. The reduction process takes a long time by using simply the reducing agent sodium borohydride [24,25]. In the present work a catalyst has been investigated for the reduction of 4-NP to 4-AP using sodium borohydride as reducing agent in aqueous medium at room temperature which is comparatively simple, efficient and greener process. The synthesized samples have been characterized and its catalytic activity has been tested for the reduction of 4-nitrophenol to 4-aminophenol using $NaBH_4$.

NiO nanoparticles have been synthesized by different methods such as solvothermal [4], microemulsion [5], microwave plasma [7], hydrothermal [15], sol–gel [18], ultrasonic [26], solid state [27], combustion [28], mechanochemical [29], thermal decomposition [30], reverse-micellar [31], electrospinning [32], vapor deposition [33] and spray pyrolysis method [34]. The various preparation methods yield diverse morphologies of NiO nanoparticles such as nanoflakes [15], nanotubes [17], nanospheres [35], nanosheets [36], nanofibers [37], nanoplatelets [38], nanodisks [39], nanorods and nanocubes [40]. But, the reported experimental techniques are still limited in laboratory scale due to some insurmountable problems and also need special conditions, tedious procedures, complex apparatus, low-yield and high-cost. The most important disadvantages of the high temperature process are that the products obtained generally possess, low surface area, inhomogeneity and agglomerated particles [41]. The homogeneous precipitation route has been used by a few authors [12,42,43]. Rai et al. [12] used microwave irradiation for its synthesis which required high calcination temperature (600 °C for 3 h), Karthik et al. [42] employed polyethylene glycol as a surfactant, while Bayal and Jeevanandam [43] required long precipitation time (6 h) for its synthesis. The present authors utilized homogeneous precipitation method at low calcination temperature (350 °C for 2 h) without using any surfactant, chelating agent, gelating agent and microwave irradiation. The homogeneous precipitation method has an easy control of uniform particle size and is environmental-friendly in preparing samples at low temperature in short time in large batch production. The calcination temperature was varied to investigate its effect on the morphology, crystallinity, specific surface area, total pore volume and optical band gap of the synthesized samples.

2. Experimental

2.1. Materials

Nickel (II) acetate ($Ni(CH_3COO)_2{\cdot}4H_2O$) (98%, ALDRICH®), ammonia solution (25%, RANKEM®), 4-nitrophenol (SRL®) and $NaBH_4$ (HIMEDIA®) were used as reagents as received without further purification. All solutions were prepared in Millipore® water.

2.2. Synthesis of nanocrystalline NiO

In this study nanocrystalline NiO powder was prepared using proper precursor by homogeneous precipitation method. The details of procedure are as follows: