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Microwave assisted synthesis of nickel nanostructures by hydrazine reduction route: Effect of solvent and capping agent on morphology and magnetic properties

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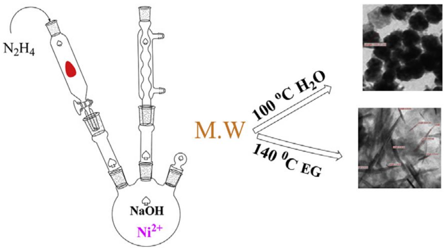
HIGHLIGHTS

- Microwave assisted synthesis of Ni nanostructures by hydrazine route is reported.
- Effect of CTAB on the properties of resulting products is reported.
- Reaction in ethylene glycol in presence of CTAB results in 1D nanorods.
- Reaction in aqueous medium results in spherical nanostructures.
- Pertinent reduction mechanism is discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

The hydrazine reduction is one of the simplest and widely used method for the synthesis of nickel nanostructures. However, large-scale production of highly monodisperse nanoparticles with desired features is difficult to achieve using this method. In this study, we report, an evaluation of microwave assisted hydrazine reduction process and the effect of solvents namely water and ethylene glycol and capping agent thereupon. The study revealed that the reaction in the former failed to give the product when hydrazine (N_2H_4) and nickel Ni(II) are in the stoichiometric molar ratio, while the reaction in the later shows that the presence of the capping agent has pronounced effect on the morphology and magnetic properties of the product. Reaction in ethylene glycol in the presence of CTAB, gave 1D nanorods of about 100 nm in length and 4–6 nm in diameter, while in the absence of CTAB highly agglomerated spheres, are obtained. The magnetic property studies indicated the ferromagnetic nature of the product. The magnetic properties are, also affected by capping agent. In both, aqueous and ethylene glycol media, the product obtained exhibit lower saturation magnetization, whereas the product obtained in ethylene glycol with CTAB has highest saturation magnetization, 47.86 emu g^{-1}.

1. Introduction

The development of facile, sustainable synthetic methods for the large-scale synthesis of well-defined monodisperse nanoparticles with small size and narrow size distribution is of crucial importance [1–3]. Keeping in view the desired properties of the resulting nanostructures in conjunction with the economic aspects of the process, the chemical reduction method in aqueous solution is investigated extensively as the best way to prepare nickel nanostructure materials [4–12]. However, the range of useful

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reducing agents is narrow and includes borohydride, sodium hypophosphite, and hydrazine. The use of borohydride, sodium hypophosphite gives the contaminated products [13], but hydrazine hydrate releases only gases as reaction product which obviates the problem of product contamination. Although the hydrazine reduction route for synthesis of nickel nanoparticles is highly explored [14–20], and considerable success has achieved in the fabrication of Ni nanoparticles using hydrazine as reducing agent, the process is associated with several demerits.

The reduction of Ni^{2+} to metallic Ni progresses through the formation of nickel hydroxide. The color change of reaction mixture from pink to green followed by black indicates the formation of nickel hydroxide as intermediate. Therefore, the direct use of metal hydroxide as a starting material is also plausible, so that the quantity of reducing agent required can be minimized. However, the hydroxide of this metal is very labile and difficult to prepare. The presence of alkaline environment is vital for the reaction; the addition of excess hydrazine to raise the pH of the solution is not effective to initiate the reaction [10]. The kinetic analysis shows that only 5% of hydrazine is utilized for the reduction of the metal ion, the remaining N_2H_4 undergoes decomposition to N_2 and H_2, in addition the disproportionation hydrazine to N_2 and NH_3 catalyzed by the product nickel nanoparticles. The reaction orders with respect to Ni^{2+}, N_2H_4 were found to be one, zero respectively. Thus, increase of the initial concentration of Ni^{2+} is ought to decrease the consumption of N_2H_4 [21] but on the other side the higher concentration of precursor results in the loss of control over the size of the product formed. The role of NaOH and its concentration dependence is also unsettled conflict [10]. Low precursor concentration, mandatory excess use of hydrazine and prolonged stirring [22,23] are not encouraging factors for the scaling-up of the process. In the majority of reported cases, products obtained are either highly aggregated spheres or microstructures of different morphologies. Moreover, most of the reactions were carried out using conventional heating or under high pressure and temperature in closed vessel reactors. These methods gave the product of poorly defined morphology, and lack scalability; therefore, faster and scalable production of fine nickel nanostructures by hydrazine reduction remains a challenge. The effect of microwave irradiation in an open vessel reactor, solvent and capping agent on the features of the resulting product remained unexplored. Keeping this in view, the hydrazine reduction route for synthesis of Nickel nanostructures under microwave irradiation is studied and results are corroborated in the following discussions.

The synthesis of nanostructures of magnetic metals by conventional methods has the major drawback of complicated procedures due to pyrogenic nature and agglomeration of the product formed [24–26]. The microwave-assisted synthesis is a sustainable option due to its ability to produce nanoparticles within a short time scale. It offers certain advantages over traditional heating methods. The coupling of permanent dipole moments of molecule with high frequency electromagnetic radiation causes resonance absorption and relaxation whereby the electromagnetic energy is converted into thermal energy. This heat is generated from inside, the material in contrast to the traditional heating where heat is transferred from outside to the inside [27–29]. The efficient energy transformation and uniform temperature distribution in reaction vessel warrant shortening of reaction time from hours to minutes, the selective formation of one phase over another is an added advantage. Consequently, Microwave irradiation is becoming an increasingly popular method for one-pot synthesis of nanomaterials. The literature survey revealed that there are very few reports pertaining the microwave assisted synthesis of Nickel nanostructures [30–33]. Further microwave assisted polyol method of Ni nanostructure synthesis was also studied [22,34,35]. These methods require the addition of several reagents or nucleating agents, in addition to the product obtained is either of poor morphology or isotropic. In this study, we report the effect of medium and capping agent on the microwave-assisted synthesis of Nickel nanostructures. Due to high dielectric tangent loss ethylene glycol (1.350), is greener solvent next to water (0.123) [36]. Modern microwave systems offer control over a wide range of experimental parameters and fine control over the growth is possible. The novelty of the work encompasses avoiding the use of excess reagents, and easily adopted for large-scale synthesis.

2. Materials and equipment's

All chemicals used in this experiment were of A.R grade and used as received without further purification. Nickel (II) chloride hexahydrate $NiCl_2$; $6H_2O$, ethylene glycol were purchased from HiMedia. Hydrazine monohydrate N_2H_4:H_2O (99–100%), cationic surfactant cetyltrimethylamonium bromide (CTAB), NaOH was purchased from Merck India. Wet chemical synthesis was carried out in microwave synthesis workstation MAS II Sineo Microwave Chemistry Technology (Shanghai). The microwave workstation is equipped with power auto-adjust function based on reaction temperature, having capability to generate non-pulse continuous microwave power for maximum microwave effect under specific reaction condition.

2.1. Characterizations

2.1.1. XRD analysis

XRD Analysis -The crystal structure determination was done by X-ray diffractiometer (Rigaku, miniflex II) using Cu Kα ($\lambda = 1.5418$ A°) radiation at the scan rate of 2 min^{-1} in the range of 2θ- 10/20 to 80°.

2.1.2. Transmission electron microscopy (TEM)

TEM observations were performed on TEM (PHILIPS model CM 200) operated at an accelerating voltage at 100 kV. Sample for TEM analysis was prepared by loading a drop of diluted isopropyl alcohol dispersion on the carbon coated copper grid. Before TEM analysis, the grid was dried under an IR lamp for 1 h.

Magnetic property measurements of the products were performed with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design). M(H) measurements were carried out at 300 K while M(T) (ZFC-FC) curves were recorded in at 50 mT with temperature increasing from 5K to 300K. Coercivity, remanance magnetization, and saturation magnetization were determined from field dependent magnetization curves.

3. Experimental

3.1. Synthesis of nickel nanostructures in aqueous medium

The reduction reactions were carried out by adjusting N_2H_4/Ni^{2+} ratio, with slight modification in the processes [37]. To the boiled and cooled aqueous solution of Nickel (II) salt (0.05 M $NiCl_2$; $6H_2O$) in three neck round bottom flask equipped with a reflux condenser, hydrazine hydrate was added drop wise through the addition funnel under continuous stirring till deep blue color is obtained. To this, an appropriate amount of NaOH (2M) was added to adjust the pH of the solution to 12. The reaction mixture was refluxed at 100 °C for 10 min under microwave irradiation at power output 500 W. After cooling, the black/green product was centrifuged at 12000 rpm using Eppendorf (5810R) cold centrifuge, the pellet obtained was washed with double distilled water, and dried in vacuum desiccator. The same experiment was repeated with the