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Synthesis and Characterization of Bimetallic CuNi, CuNi$_2$ and CuNi$_3$ Nanoparticles

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Abstract: Bimetallic CuNi nanoparticles of varying composition (1:1, 1:2, and 1:3) have been successfully synthesized by chemical reduction of metal chlorides with hydrazine at room temperature without any protective agent and inert gas protection. This synthetic method is proven to be very simple and facile. The X-ray diffraction (XRD) patterns of CuNi alloy nanoparticles of different compositions show the characteristic peaks of CuNi alloys with face centered cubic structure and their crystallite size between 46-57nm. Using Scanning Electron microscopy (SEM) and Energy dispersion X-ray analysis (EDAX), the morphology and the elemental composition of varying ratios were determined. The magnetic measurements revealed the synthesized nanoalloys exhibit the ferromagnetic behaviour for all the ratios.

Keywords: Nanoparticles, X-ray diffraction, Lattice parameter, Magnetic properties.

Introduction

Currently, much attention has been focused on the preparation of magnetic nano-materials because of their potential application in Ferro-fluids, advanced magnetic materials, catalysts, optical and mechanic devices, high density magnetic recording media and medical diagnostics [1-3]. The bimetallic nanostructures have recently received much research attention due to their unique physicochemical properties. As compared to monometallic counter parts, the bimetallic nanoparticles present a large number of attractive properties such as an electrochemical catalyst and photo catalyst. However, the high chemical activity is a forcible constraint facing wide utilization of this new class of materials. Among the reported nanostructures, CuNi nanoalloys have been extensively studied as a catalyst and electro catalyst in different reactions such as carbon nanotubes formation, fuel cells, and hydrogen release from sodium borohydride [4-6]. The binary alloy CuNi shows a promising magnetic phase transition in the desired range of temperature for hyperthermia treatment of cancer [7]. Ni-based bimetallic nanoparticles containing copper have gained considerable interest in the last decade due to the high catalytic conversion and selectivity properties[8] and potential magneto resistance materials[9].

Several methods have been reported, such as Sol-gel [10], solution chemical reduction [11], organometallic precursor thermolysis [12], and chemical vapour deposition [13]. Among these methods, I have chosen chemical reduction method to synthesize the CuNi nanoparticles. Researchers synthesized various nanoparticles using inert atmosphere. But, this method is simple, more facile and no inert atmosphere has been used. CuNi Nanoparticles has been synthesized at low temperature particularly at 55°C.

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Experimental

All the chemicals of reagent grade quality were used without further purification; including Copper chloride hydrate ($CuCl_2.2H_2O$), Nickel Chloride hexahydate ($NiCl_2.6H_2O$), Sodium hydroxide (NaOH), Ethylene glycol ($C_2H_6O_2$) and Hydrazine hydrate ($N_2H_4.H_2O$). CuNi bimetallic nanoparticles of various ratios (1:1, 1:2, 1:3) were prepared by hydrazine reduction method using ethylene glycol as reported earlier [14-16]. An appropriate amount of metal chlorides of different ratios was dissolved in universal solvent followed by addition of 3ml of hydrazine hydrate, ethylene glycol and required amount of sodium hydroxide (1M) was added with continuous stirring by maintaining the pH around 11.5 at 55 ° C. The formed nanoparticles were collected, washed, filtered and dried at room temperature.

The average crystallite size of the nanopowders were analyzed using powder x-ray diffractometer using CuKα (λ = 1.5418 Å) radiation. The morphology and structure of the sample was characterized by scanning electron microscopy (SEM). The elemental composition of bimetallic nanoparticles was determined from energy dispersive x-ray spectra (EDS). Room temperature magnetic measurements were carried out using vibrating sample magnetometer (VSM) and various parameters were evaluated.

Results and Discussion

The XRD patterns of the bimetallic CuNi nanoparticles with various ratios (1:1, 1:2, 1:3) are given in Fig. 1. All the samples are assigned to face cubic structures from the diffraction lines of (111), (200), (220) and (311) planes in the XRD profile. It is already known to us that both copper and nickel possess an fcc structure.
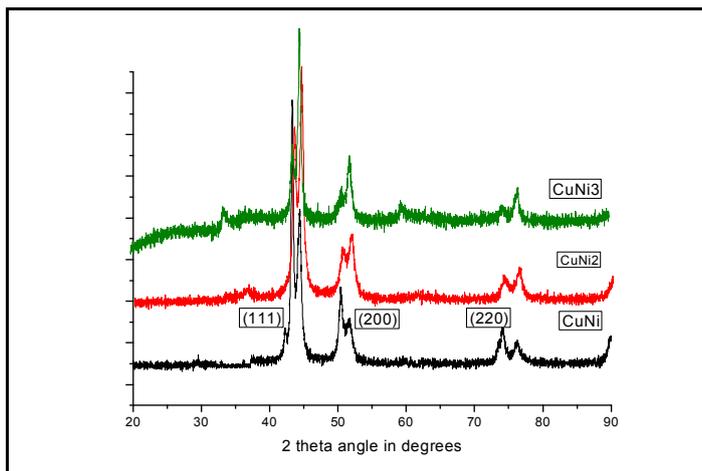

Fig.1. XRD pattern of the CuNi (1:1, 1:2, 1:3) nanoparticles

The crystallite size of the nano-crystalline samples was measured using Debye-Scherer formula[17],

$$D_{XRD} = 0.98\lambda/\beta \cos\theta$$

Where λ is the wavelength of X-ray used in Å, β is the full width at half-maximum (FWHM) in radians in the 2θ scale, θ is the Bragg angle, D_{XRD} is the crystallite size in nm. The value of D decreases from 57 to 46nm on increasing value of nickel. The lattice constant (a) was computed using the 'd' value and with their respective (hkl) parameters. . The lattice constant calculated using the equation given below and tabulated in Table 1.

$$a = d (h^2 + k^2 + l^2)^{1/2}$$

Table 1 XRD parameters of $Ni_{1-x}Cd_xFe_2O_4$ powders

Ratio	Chemical Formulae	2θ	d-spacing	Lattice constant 'a' in Å	AverageParticle size 'D' in nm
1:1	CuNi	43.6066	2.0745	3.5932	57.302
1:2	$CuNi_2$	44.136	2.0508	3.5521	49.6613
1:3	$CuNi_3$	44.4285	2.0378	3.5296	46.7807

The lattice parameters determined by XRD measurements are found to decrease with increase in nickel contents, going from 3.5932 to 3.5296 Å. The lattice parameters of all the ratios are located in between the corresponding lattice parameter of pure Ni is 3.517 Å (4-850 JCPDS card) and pure Cu is 3.615 Å (4-836 JCPDS card). With the increase of nickel content, the diffraction lines are shifted to high angle and more close to the position of pure Nickel. As in the case of (111) plane, the diffraction peak of CuNi, $CuNi_2$, $CuNi_3$ of 43.6066, 44.136, 444.4285 respectively, shows a slight shift from low angle to high angle with increase of nickel content in the composition. The shift of diffraction lines is due to the formation of CuNi alloy, instead of core/shell structure, because it will not show such a shift [18]. Furthermore, no peaks corresponding to pure copper and pure nickel are present in the XRD patterns, thereby excluding the possibility that the as-synthesized nanoparticles were simply the mixtures of the two metal nanoparticles.

The Scanning electron microscopic image of the CuNi nanoparticles of various ratios along with the energy dispersive X-ray spectroscopic analysis (EDX) is shown in Fig. 2. The average composition of CuNi is of approximately matches with the uniform distributions of elements suggests that the prepared product is indeed in the form of CuNi, $CuNi_2$, $CuNi_3$. Hence the complete reduction of Cu and Ni from their corresponding ionic states to the metallic state has been taken place.
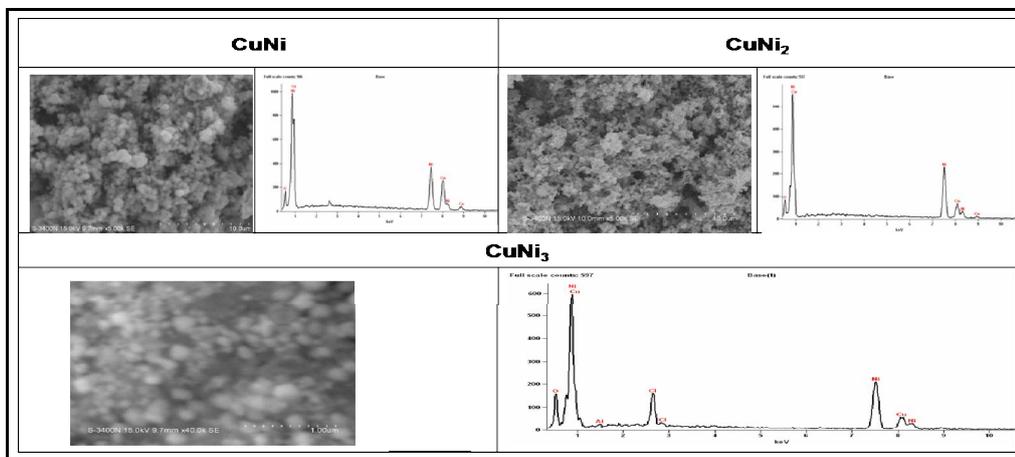

Fig.2 SEM and EDX images of CuNi (1:1, 1:2, 1:3) nanoparticles

The magnetic properties of the CuNi nanoparticles of various ratios were studied using vibrating sample magnetometer (VSM) and their magnetic hysteresis curves (M-H) were shown in Fig. 3.
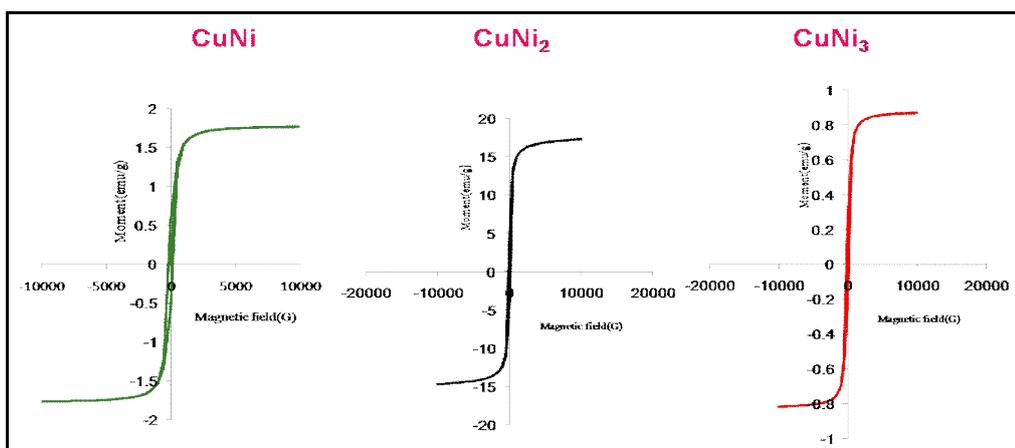

Figure 3 M-H Curves of CuNi (1:1, 1:2, and 1:3) nanoparticles

Using M-H curves, Saturation magnetization (Ms), Coercivity (Hc) were calculated and tabulated in the Table 2.

Table 2 Magnetic properties of CuNi nanoparticles

x	Chemical Formulae	Coercivity H_c (KOe)	Magnetization M_s (emu/gm)
1:1	CuNi	12	1.626
1:2	$CuNi_2$	10.6	15.998
1:3	$CuNi_3$	11	42.516

The saturation magnetization increases obviously with increase of nickel content, since the magnetic property of nickel is higher than the copper. We already know that nickel is ferromagnetic material and its strong magnetic property results from the super exchange interaction between the free electrons within the nickel atom. Since the super exchange interaction is strengthened with distance of nickel atom, the saturation magnetization of CuNi alloy is enhanced with increase in nickel content. The Coercivity (Hc) values differ from 10 to 12KOe.

Conclusion

The CuNi bimetallic nanoparticles of different ratios have been successfully synthesized at room temperature without using any protective agent and inert atmosphere. The XRD spectrum predicts the formed CuNi of ratios (1:1, 1:2, 1:3) BMNs is face centered cubic structure. The lattice parameter is found to decrease with increase in nickel concentration and which is in between the values of pure Cu and Pure Ni, which confirms the formation of bimetallic nanoparticles. We synthesized CuNi nanoparticles with increasing nickel content, which shows the ferromagnetic behavior and it is also confirmed through VSM spectrum. The method we synthesized is very simple, low cost, easy to operate and relatively cheap and eco-friendly.

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