

## Research Article

# Mild Hydrothermal Synthesis of Ni–Cu Nanoparticles

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Magnetic Ni-rich Ni–Cu nanoparticles with Ni : Cu mass ratio ( $S$ ) of 2.0 and 2.6 were prepared using a mixture of polyoxyethylene (10) isooctylphenyl ether (Triton X-100) and sodium dodecyl sulfate (SDS) in a mild hydrothermal condition at 95°C. X-ray diffractometry (XRD) showed that the nanoparticles prepared at  $S = 2.0$  possessed Ni–Cu alloy characteristic whereas the characteristic was absent at  $S = 2.6$ . The XRD data was enhanced by Fourier transform infrared spectroscopy (FTIR) which exhibited metal-metal (Ni–Cu) band at 455  $\text{cm}^{-1}$ . Based on transmission electron microscopy (TEM), the average particle sizes for the nanoparticles prepared at  $S = 2.0$  and 2.6 were in the range of 19–23 nm. The as-prepared nanoparticles exhibited paramagnetic behaviour measured using a vibrating sample magnetometer (VSM) and the specific saturation magnetization decreased at the higher concentration of Ni.

## 1. Introduction

Magnetic materials in the form of nanoparticles have received a lot of attention because of their unique magnetic properties, which are dominated by superparamagnetism. These materials can be used in a broad range of applications, including the production of magnetic fluids. Magnetic fluids are produced by dispersing the superparamagnetic nanoparticles in a carrier liquid. These magnetic fluids have potential application in various modern technologies ranging from medicines and pharmaceuticals to electronics and mechanics [1]. As magnetic properties of nanoparticles are dominated by particle size, it is important to control the particle size, size distribution, as well as the morphology of the particles during the synthesis process.

Ni-based bimetallic nanoparticles containing Cu have gained considerable interest in the last decade due to the high catalytic conversion and selectivity properties [2] and potential giant magnetoresistance materials [3]. In the recent years, Ni–Cu alloy nanoparticles have been proposed as mediator for magnetic fluid hyperthermia [4–6]. Several

methods have been reported for the preparation of Ni–Cu nanoparticles including sol-gel [7], reduction of mixture of Ni and Cu compounds under hydrogen [8], evaporation of Ni–Cu alloy and cocondensation with organic solvents [9], water-in-oil microemulsion [10], solvothermal [11], and hydrothermal [12].

In this work, we report on the synthesis of Ni–Cu nanoparticles by polymer-surfactant-mediated hydrothermal processing route at a fairly low temperature of 95°C, in which metal ions were localized by the polymer-surfactant association and reduced the metal ions to nanometer size [12].

## 2. Experimental

All reagents were of analytical grade and used as received from Sigma Aldrich. The synthesis method was similar to that described by Niu et al. [12]. Briefly, 0.67 g nickel acetate and 0.33 g copper acetate, which gave a mass ratio ( $S$ ) of 2.0, were added into 40 mL distilled water containing 0.16 g

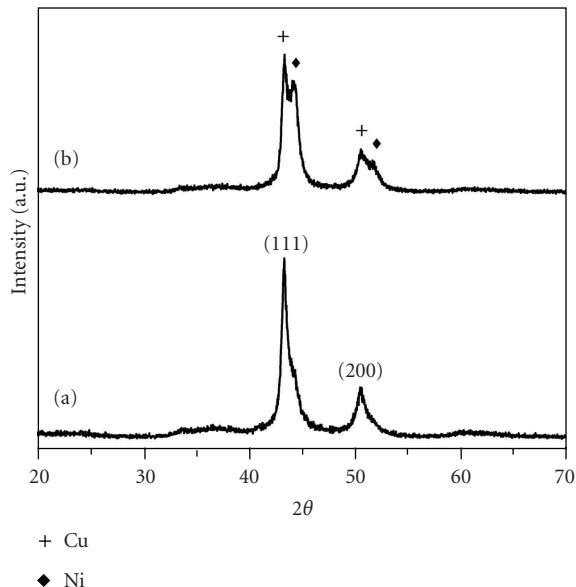


FIGURE 1: XRD patterns of (a) Ni-Cu alloy ( $S = 2.0$ ) and (b) bimetallic Ni-Cu ( $S = 2.6$ ).

sodium dodecyl sulfate (SDS) and mixed at room temperature. Then, 1.0 mL polyoxyethylene (10) isooctylphenyl ether (Triton X-100) and 1.0 mL ammonia solution were added into the mixture. This was followed by adding 4.0 mL 80 wt% hydrazine hydrate solution into the mixture after strong stirring for 30 minutes. The mild hydrothermal was carried out by pouring the mixture into a SCHOTT glass bottle with 100 mL capacity, closed tightly and put into an oven at the temperature of  $95^{\circ}\text{C}$  for 4 hours. The resulting black precipitate was separated using a centrifuge and washed several times with ethanol and distilled water to remove the remaining surfactants. The product was dried in an oven at  $60^{\circ}\text{C}$  for 24 hours. In the same way, the mixture with  $S = 2.6$  was prepared with 0.72 g of nickel acetate and 0.28 g of copper acetate.

The samples were characterized by a Bruker AXS-D8 Advance X-ray powder diffractometer (XRD) using a scanning rate of  $0.025^{\circ}\text{s}^{-1}$  in a  $2\theta$  range from  $20^{\circ}$  to  $70^{\circ}$  with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). The micrographs were taken using a LEO 12CB transmission electron microscopy (TEM). The atomic ratio of Ni to Cu was determined by an energy dispersion X-ray analysis (EDXA) which was performed on a LEO 1450 vapour pressure scanning electron microscopy (SEM). The chemical bonding of the samples was observed using a Perkin Elmer GX Model Fourier transforms infrared spectrometer (FTIR). Magnetic hysteresis loops were measured on a vibrating sample magnetometer (VSM) (Lake Shore 4700).

### 3. Results and Discussion

The XRD data of the samples prepared with  $S = 2.0$  and  $2.6$  is displayed in Figure 1. Figure 1(a) shows that the sample prepared with  $S = 2.0$  is an alloy, which is in

TABLE 1: EDXA of Ni-Cu alloy ( $S = 2.0$ ) and bimetallic Ni-Cu ( $S = 2.6$ ).

Element	Ni-Cu alloy ( $S = 2.0$ )		Bimetallic Ni-Cu ( $S = 2.6$ )	
	Wt%	Atomic%	Wt%	Atomic%
Ni	38.68	15.83	46.92	21.81
Cu	20.64	7.81	20.48	8.80

agreement with Niu et al. [12]. The diffraction peaks (111) and (200) are indexed to JCPDS No. 47-1406, which shows the characteristic of an alloy. There were no observable lines in the XRD pattern corresponding to pure Cu or Ni. On the contrary, the sample prepared with  $S = 2.6$  shows the XRD pattern of pure Ni and Cu, which corresponds to JCPDS No. 4-0850 and 4-0836, respectively. Based on the XRD results, an alloy of Ni-Cu could be obtained with  $S = 2.0$  whereas an alloy does not form at the higher concentration of Ni.

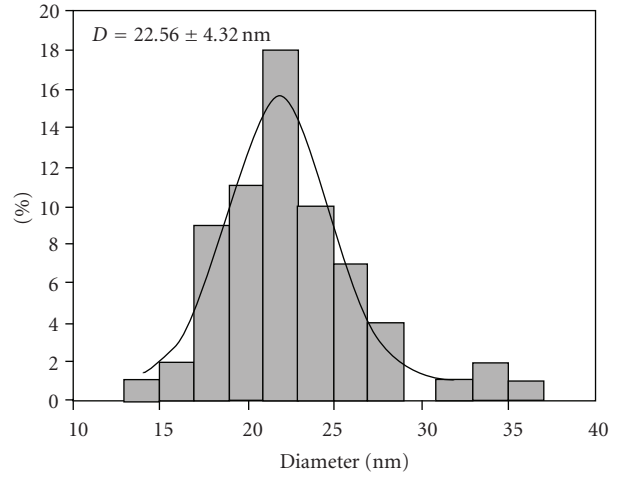
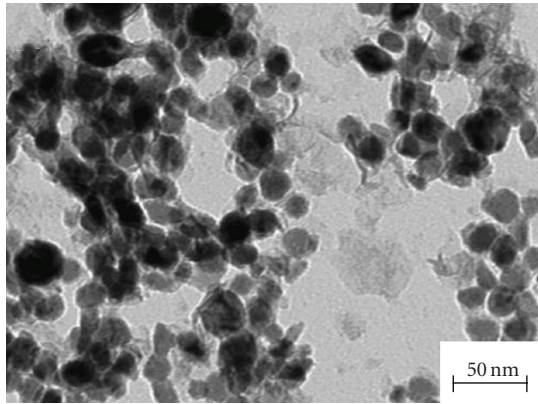
The size of coherently scattering domains (i.e., the crystallite size,  $D$ ) of Ni-Cu alloy ( $S = 2.00$ ) is approximately 8 nm. The calculation is based on the full width at half maximum (FWHM) of diffraction peak from (111) plane using Debye-Scherrer's equation

$$D = 0.98\lambda \frac{1}{\beta \cos \theta}, \quad (1)$$

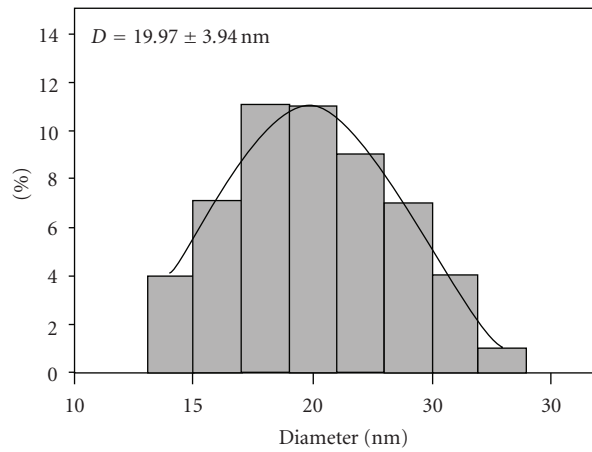
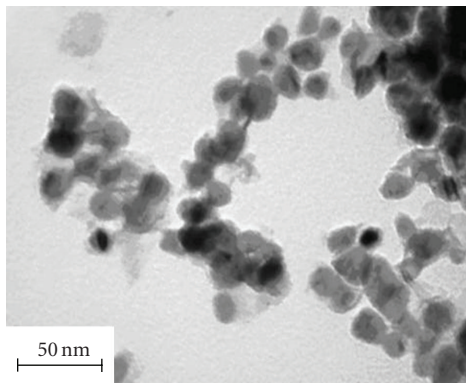
where  $D_{\text{hkl}}$  is the average crystallite size,  $\beta$  is the broadening of FWHM of the main intense peak (111) in radian,  $\theta$  is the Bragg angle, and  $\lambda$  is the radiation wavelength. The estimated value is much smaller than that of the TEM observation as shown in Figure 2. The particles are uniformly dispersed and spherical in shape. The mean diameter obtained from measurement for Ni-Cu alloy ( $S = 2.0$ ) and bimetallic Ni-Cu ( $S = 2.6$ ) is  $22.56 \pm 4.32 \text{ nm}$  and  $19.97 \pm 3.94 \text{ nm}$ , respectively. A plausible explanation is that the nanoparticles are attracted to one another via magnetism, and thus, the attraction aggregates the nanoparticles into much larger particles. The lattice parameter of the Ni-Cu alloy ( $S = 2.0$ ) is  $3.586 \text{ \AA}$ , which is consistent with Niu et al. [12]. The Ni-Cu ratios are consistent with the values obtained from energy dispersive X-ray analysis (EDXA) as shown in Table 1.

The observed FTIR spectra of the as-synthesized nanoparticles are shown in Figure 3. The bands at  $1598$ ,  $1375$ ,  $664$ , and  $548 \text{ cm}^{-1}$  can be attributed to the vibration characteristic of Triton X-100. The band at  $1384 \text{ cm}^{-1}$  is assigned to  $-\text{CH}_3$  symmetric deformation of Triton X-100. The band at  $3420 \text{ cm}^{-1}$  is assigned to the stretching vibration of  $-\text{OH}$  group, which may be present due to adsorbed water molecule. The band at  $455 \text{ cm}^{-1}$  corresponds to the stretching vibration of metal-metal (Ni-Cu) band [2]. There is no characteristic band that can be attributed to  $\text{Cu-O-C}$  or  $\text{Ni-O-C}$ , which suggests that there is no strong interaction between Ni-Cu nanoparticles and Triton X-100.

The room temperature magnetic properties of the Ni-Cu nanoparticles, measured in an applied magnetic field of  $10^4 \text{ G}$ , are depicted in Table 2. From the hysteresis loop shown in Figure 4, squareness ( $R$ ), the ratio of the remanence to the saturation magnetization is derived to determine



(a)



(b)

FIGURE 2: TEM images (left) and particle size distribution (right) of (a) Ni-Cu alloy ( $S = 2.0$ ) and (b) bimetallic Ni-Cu ( $S = 2.6$ ).

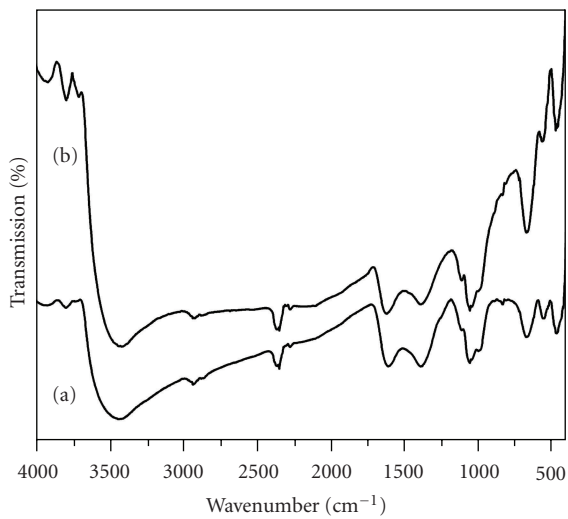


FIGURE 3: FTIR spectra of (a) Ni-Cu alloy ( $S = 2.0$ ) and (b) bimetallic Ni-Cu ( $S = 2.6$ ).

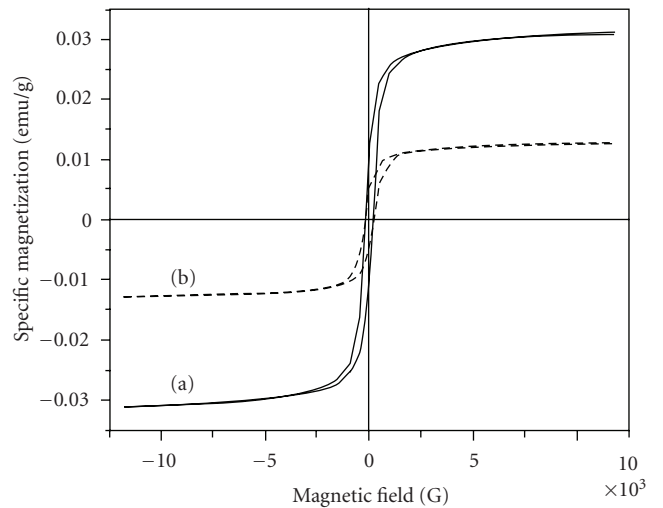


FIGURE 4: M-H hysteresis loops of (a) Ni-Cu alloy ( $S = 2.0$ ) and (b) bimetallic Ni-Cu ( $S = 2.6$ ).

TABLE 2: Magnetic properties of Ni–Cu alloy ( $S = 2.0$ ) and bimetallic Ni–Cu ( $S = 2.6$ ).

Sample	Squareness	Saturation magnetization, $M_s$ (emu/g)	Coercivity (G)	Retentivity (emu/g)
Ni–Cu alloy ( $S = 2.0$ )	0.326	14.695	178.84	4.791
Bimetallic Ni–Cu ( $S = 2.6$ )	0.305	13.565	190.82	4.134

whether the intergrain exchange exists [13]. Stoner and Wohlfarth have reported that  $R = 0.5$  suggests randomly oriented noninteracting particles undergoing coherent rotation while  $R < 0.5$  shows that the particles interact by magnetostatic interaction [14]. The exchange-coupled exists when  $R > 0.5$ . Since the as-synthesized nanoparticles both show values of  $R < 0.5$  these nanoparticles interact by magnetostatic interaction. Ni–Cu alloy ( $S = 2.0$ ) shows greater value of magnetization than bimetallic Ni–Cu ( $S = 2.6$ ). The lower  $M_s$  value associated to the bimetallic Ni–Cu nanoparticles is attributed to two factors. Firstly, surface distortion is due to oxidation of magnetic bimetallic Cu–Ni, and this effect is especially prominent due to their large surface-to-volume ratio [15]. Secondly, the magnetocrystalline anisotropy of the nanoparticles depends on the degree of crystallinity of nanoparticles. As observed in XRD, bimetallic Ni–Cu is partially crystalline, which suggests that a large portion of the crystals is defect as dislocations can occur within the lattice. This will cause a significant reduction in magnetic moment within the nanoparticles as a result of magnetocrystalline anisotropy distortion. The coercivity,  $H_c$ , of Ni–Cu alloy and bimetallic Ni–Cu nanoparticles is 178.84 and 190.82 G, respectively. These low values indicate that the magnetic nanoparticles have a tendency to be in a paramagnetic state due to its small diameter.  $H_c$  is the main technical parameter to characterize the magnetism of magnetic nanoparticles, in which this value is strongly size dependent [16].

## 4. Conclusions

Under mild hydrothermal conditions, Ni–Cu nanoalloy with diameter of about 22 nm was successfully prepared at 95°C using Triton X-100 and SDS. Simultaneous reduction and concentration of Ni and Cu are vital factors to form Ni–Cu nanoalloy. When  $S = 2.6$ , a homogeneous alloy could not be formed due to depletion effect. Ni–Cu nanoalloy shows paramagnetism at 25°C, which decreased with increased Ni.

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