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# Magnetic nanofilms of nickel prepared at the liquid-liquid interface

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## 1. Introduction

Magnetic nanomaterials are of value due to their potential applications in magnetic fluids, magnetic storage, biomedical applications and catalysis [1–4]. In this context, nickel nanostructures have been prepared by various methods employing sputtering, pyrolysis, aqueous and nonaqueous chemical reduction, sonochemical deposition and water-oil microemulsions [5-9]. Huo and Gao [10] prepared Ni nanoparticles by the reduction of nickel acetylacetonate with sodium tetrahydridoborate in the presence of hexadecyl amine and studied their magnetic properties. The synthesis of hcp Ni nanoparticles in polyethylene glycol under refluxing conditions in the presence of oleic acid and oleyl amine has been reported by Tzitzios et al. [11]. Reduction of nickel acetylacetonate by hydrazine in oleyl amine also yields hcp or a mixture of hcp and fcc Ni nanoparticles depending on the reaction temperatures [12]. Synthesis and magnetic properties of singlecrystalline nanorods and ultra-thin sheets of nickel prepared by the decomposition of nickel acetate in the presence of long-chain amines under solvothermal conditions have been reported by Ghosh et al. [13]. Han et al. synthesized Ni nanoparticles with fcc and hcp structures by the thermal decomposition of Ni oleate in dodecylamine and octadecene system [14]. Ni nanobelts have been obtained by the reduction of a Ni tartrate complex under surfactant-assisted hydrothermal conditions [15].

#### ABSTRACT

Thin films of metallic nickel with a thickness of the order of 20 nm have been prepared at the organicaqueous interface at room temperature by the reaction of nickel cupferronate  $[Ni(C_6H_5N_2O_2)_2]$  in toluene medium and sodium borohydride (NaBH<sub>4</sub>) in aqueous medium. The films were characterized with transmission electron microscopy, scanning electron microscopy and atomic force microscopy. Thicker Ni films could be prepared by carrying out the reaction at the interface at 60 °C. The Ni nanofilms exhibit superparamagnetic behavior.

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Most of the synthetic methods for Ni nanostructures reported in the literature use high temperature, surfactants, or long chain amines. It was our interest to prepare Ni nanostructures at room temperature in the absence of any surfactants or amines. For this purpose, we have employed the organic–aqueous interface to prepare thin films of nickel. The organic–aqueous interface has been used to generate various nanostructures, specially single crystalline films of inorganic materials [16]. In this article, we report the synthesis and characterization of nickel nanosheets prepared by the interface reaction between nickel cupferronate in toluene medium and sodium borohydride in the aqueous medium.

## 2. Experimental

Nickel nanofilms were prepared by the reaction of nickel cupferronate  $(Ni(Cup)_2, Ni(C_6H_5N_2O_2)_2)$  as the nickel source and sodium borohydride (NaBH<sub>4</sub>) as the reducing agent. Ni(Cup)<sub>2</sub> was prepared by the reaction of nickel acetate and cupferron at 0 °C. The product formed was filtered, washed with water and dried at 40 °C in an oven. In a typical reaction, 25 mL of 0.1 mM of Ni(Cup)<sub>2</sub> in toluene was added slowly to 25 mL of 5 mM of NaBH<sub>4</sub> in water. The interface that formed between the two layers turned silverish white after a few hours. The interface was kept undisturbed for 30 h for the growth of the nickel nanofilm to occur. The film formed at the interface was lifted onto a silicon substrate for characterization. The film was taken on a holey carbon grid for transmission electron microscopic (TEM) measurements and on a quartz plate for UV-vis spectroscopic measurements. To examine the effect of temperature on the formation of the film, the reaction was carried out at 60 °C keeping the other conditions same.

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Fig. 1. (a) FESEM and (b) TEM images of a nickel film formed at the liquid-liquid interface at room temperature. Inset in (b) shows a SAED pattern of the film. The scale bar in the inset is 20  $\mu$ m.

Field emission scanning electron microscope (FESEM) images were recorded with a FEI NOVA NANOSEM600. Transmission electron microscope (TEM) images were obtained with a JEOL (JEM3010) transmission electron microscope operating with an accelerating voltage of 300 kV. UV–vis absorption spectrum was recorded with a Perkin-Elmer Lamda 900 UV/VIS/NIR spectrometer. Atomic force microscope (AFM) measurements were performed with Innova atomic force microscope. Magnetic measurements were carried out with a vibrating sample magnetometer in Physical Properties Measurement System (PPMS, Quantum Design, USA).

#### 3. Results and discussion

In Fig. 1a, we show a FESEM image of a typical nickel film formed at room temperature (30  $^{\circ}$ C) at the interface. Fig. 1b shows

a TEM micrograph of a Ni film. The film is crystalline as can be seen in the selected area electron diffraction (SAED) pattern in the inset in Fig. 1b. The electron diffraction spots could be indexed on the hexagonal structure ( $PG_3/mmc$ , a = 2.651 Å, c = 4.343 Å, JCPDS No. 45-1027). The TEM image also reveals the presence of small nanoparticles with diameters in the 2–3 nm range. Slightly bigger particles (8–10 nm diameter) were also seen in some parts of the film (indicated by black arrows).

Typical AFM images of Ni films are shown in Fig. 2. The images reveal that the films are smooth and continuous over wide areas. The three-dimensional image of the film in Fig. 2a and the height profile in Fig. 2b show that the average thickness of the film is of the order of 20 nm.

Magnetic properties of the nickel film formed at the interface were measured. In Fig. 3a, we show the temperature dependence of



Fig. 2. (a) 3D AFM image of a nickel film formed at the liquid-liquid interface and (b) AFM image showing height profile of a film.



Fig. 3. (a) Temperature dependence of magnetization for a nickel film formed at the liquid–liquid interface (recorded at 100 Oe). (b) Magnetization as a function of the applied field measured at 5 K. The inset shows the enlarged magnetization curve.



Fig. 4. (a) UV-vis spectrum of a Ni film formed at the liquid-liquid interface and (b) I-V characteristics of a Ni film.



Fig. 5. (a) FESEM and (b) TEM images of a nickel film formed at the liquid-liquid interface at 60 °C.

magnetization under zero-field cooled (ZFC) and field-cooled (FC) conditions at 100 Oe. The ZFC curve shows a maximum at the blocking temperature  $(T_{\rm B})$  of 13.5 K characteristic of a superparamagnetic material. A  $T_{\rm B}$  in the range of 12–40 K has been reported earlier in the literature for nickel nanomaterials [10,17]. The ZFC and FC curves diverge below  $T_{\rm B}$ , characteristic of superparamagnetic materials [18]. The FC curve shows that magnetization continues to increase with decrease in temperature below T<sub>B</sub>. Fig. 3b shows the field-dependent magnetic behavior of a film at 5 K. The M-H curve shows hysteresis with a saturation magnetization  $(M_S)$  of 45 emu/g, which is lower than that of bulk nickel (55 emu/g). Such a reduced value of  $M_S$  is expected in a nanofilm. The coercivity at 5 K is 770 Oe whereas the coercivity above  $T_{\rm B}$  is negligible. The magnetic hysteresis disappears above  $T_{\rm B}$ , as expected of a superparamagnet [10,18,19]. The present results clearly establish that the nickel film generated at the liquid-liquid interface is superparamagnetic.

In Fig. 4a, we show the UV–vis spectrum of a nickel film formed at the interface. The spectrum shows a broad, weak feature around 320 nm due to surface plasmon resonance (SPR). There are literature reports of SPR bands of Ni nanoparticles, Ni/SiO<sub>2</sub> glass nanocomposites and Ni implanted alumina in this wavelength region [19–21]. Fig. 4b shows typical *I–V* characteristics of a nickel film. The *I–V* curve is linear indicating the metallic character of the nickel film.

Nickel films were also prepared at the liquid–liquid interface at a higher temperature to check the effect of temperature on the film characteristics. In Fig. 5a, we show a FESEM image of a film formed at the interface at 60 °C. The film appears to be rough compared to that formed at the room temperature. The TEM image of the film shows the presence of small nanoparticles (2-3 nm) as shown in Fig. 5b. An AFM image of the film formed at the interface at 60 °C is shown in Fig. 6. From the *z*-scale image of the film shown as the inset in Fig. 6, the thickness is estimated to be of the order of 30 nm. This film also exhibits a superparamagnetic behavior.



Fig. 6. AFM image of the film showing the height profile of a Ni film formed at the liquid-liquid interface at 60  $^\circ$ C.

# 4. Conclusions

In conclusion, the present study demonstrates that the organicaqueous interface can be used to generate nickel nanofilms by the interface reaction between nickel cupferronate and sodium borohydride at room temperature. The films prepared at room temperature are  $\sim 20$  nm thick and exhibit superparamagnetism. Ni films prepared at a higher temperature (60 °C) are thicker and less well formed compared to those prepared at room temperature.

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#### References

- [1] M.-P. Pileni, Adv. Funct. Mater. 11 (2001) 323-336.
- [2] S. Sun, C.B. Murray, D. Weller, L. Folks, A. Moser, Science 287 (2000) 1989-1992.
- [3] K.B. Lee, S. Park, C.A. Mirkin, Angew. Chem. Int. Ed. 43 (2004) 3048-3050.
- [4] J. Park, E. Kang, S.U. Son, H.M. Park, M.K. Lee, J. Kim, K.W. Kim, H.-J. Noh, J.-H. Park, C.J. Bae, J.-G. Park, T. Hyeon, Adv. Mater. 17 (2005) 429–434.

- [5] S.L. Che, K. Takada, K. Takashima, O. Sakurai, K. Shinazaki, N. Mizutani, J. Mater. Sci. 34 (1999) 1313–1318.
- [6] G.B. Thompson, R. Banerjee, X.D. Zhang, P.M.H.L. Anderson, Fraser Acta Mater. 50 (2002) 643–651.
- [7] S.H. Wu, D.H. Chen, Chem. Lett. 33 (2004) 406–407.
- [8] S. Ramesh, Y. Koltypin, R. Prozorov, A. Gedanken, Chem. Mater. 9 (1997) 546–551.
- [9] D.-H. Chen, S.-H. Wu, Chem. Mater. 12 (2000) 1354–1360.
- [10] Y. Hou, S. Gao, J. Mater. Chem. 13 (2003) 1510–1512.
- [11] V. Tzitzios, G. Basina, M. Gjoka, V. Alexandrakis, V. Georgakilas, D. Niarchos, N. Boukos, D. Petridis, Nanotechnology 17 (2006) 3750-3755.
- [12] Y.T. Jeon, J.Y. Moon, G.H. Lee, J. Park, Y. Chang, J. Phys. Chem. B 110 (2006) 1187–1191.
- [13] S. Ghosh, M. Ghosh, C.N.R. Rao, J. Cluster Sci. 18 (2006) 97-111.
- [14] M. Han, Q. Liu, J. He, Y. Song, Z. Xu, J. Zhu, Adv. Mater. 19 (2007) 1096-1110.
- [15] Z. Liu, S. Li, Y. Yang, S. Peng, Z. Hu, Y. Qian, Adv. Mater. 15 (2003) 1946-1948.
- [16] C.N.R. Rao, K.P. Kalyanikutty, Acc. Chem. Res. 41 (2008) 489-499.
- [17] F.C. Fonseca, G.F. Goya, R.F. Jardim, R. Muccillo, N.L.V. Carreno, E. Longo, E.R. Leite, Phys. Rev. B 66 (2002) 104406 (1–5).
- [18] T. Bala, S.D. Bhame, P.A. Joy, B.L.V. Prasad, M. Sastry, J. Mater. Chem. 14 (2004) 2941–2945.
- [19] P.K. Verma, A. Giri, N.T.K. Thanh, L.D. Tung, O. Mondal, M. Pal, S.K. Pal, J. Mater. Chem. 20 (2010) 3722–3728.
- [20] O.A. Yeshchenko, I.M. Dmitruk, A.A. Alexeenko, A.M. Dmytruk, J. Phys. Chem. Solids 69 (2008) 1615–1622.
- [21] X. Xiang, X.T. Zu, S. Zhu, L.M. Wang, Appl. Phys. Lett. 84 (2004) 52-54.