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Fabrication of Langmuir–Blodgett film from Polyvinylpyrrolidone stabilized NiCo alloy nanoparticles

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ABSTRACT

The fabrication of monolayer/multilayer films of Polyvinylpyrrolidone (PVP) stabilized NiCo alloy nanoparticles with an average particle size 7 nm via Langmuir–Blodgett method is presented in this paper. The NiCo alloy nanoparticles were synthesized in ethanol using hydrazine hydrate as reducing agent at 60 °C in the presence of PVP and washed with a mixture of chloroform–methanol (1:1) solution to get pure PVP capped alloy nanoparticles. The NiCo alloy suspension was spread to the interface of air/water and transferred to the glass surface. The formation of a Langmuir monolayer/multilayer of PVP stabilized NiCo particles at air/water interface were revealed with the pressure-area isotherm curve. The transfer of nanoparticles on the glass surface was found to be efficient for the first six layers as exhibited by the pressure-area isotherm and increases in absorption intensity in the UV–Vis range. The atomic force microscopy results show that this film has a cubic symmetry in a two dimensional (2D) array.

1. Introduction

Nowadays, a lot of advancement in the development of nanodevices based on magnetic material is being studied. The magnetic thin films are very useful in various applications like high density magnetic storage media, magneto-resistive random access memory device etc. The magnetic properties of nanoparticles are strongly dependent on the particle size, shape and the crystal structure. The research of 2D ordered arrays of nanoparticles is becoming an important factor for the development of high density magnetic recording media and single electron tunneling device. The Langmuir–Blodgett (LB) films of Au, Ag, CdS, FePt and Fe_2O_3 have been extensively investigated for their potential applications in nanodevices [1–7].

Formation of ordered thin films of uniform size nanoparticles provides a route to nanostructured materials. The LB technique has long been recognized as a powerful method since it offers a means to organize the molecules in a desired way, with the resulting LB films often possessing a high degree of packing order at the molecular level [8,9]. In the LB method, a thin molecular layer spread at the air/water interface (Langmuir monolayer) is transferred onto a solid substrate; the process can be repeated several times with the same substrate to form multilayer films [10,11]. The incorporation of "guests" in the LB films such as atoms, molecular clusters and nanoparticles are of great scientific and technological interest due to the fact that the functional properties of the films and "guest materials" are combined together [12–14]. These may lead to potentially new properties and applications as electronic, optical [15,16] and magnetic materials as well as sensor devices [17].

Control on size, shape and composition of magnetic nanoparticles are essential for diagnostic tools of cancer tumors and targeting treatment in HIV infection. The magnetic behavior of NiCo nanoparticles has been revealed as it can be used to enhance the signal from magnetic resonance imaging [18]. The synthesis of NiCo alloy nanoparticles is quite tedious as it is more susceptible for the formation of oxides than pure metal nanoparticles. A variety of techniques have been used to produce nanoparticles of Ni, Co and NiCo alloys using different synthesis approaches such as chemical and hydrothermal reductions [19,20], organic colloid method [21], thermal decomposition [22,23], laser ablation [24], microwave method [25] and sol–gel method [26]. Unfortunately however, straightforward synthesis leading to nanostructured powders of nickel; nickel–cobalt alloys are rare. Syukri et al. [27] synthesized metallic Ni and NiCo alloy fine powders from a mixed-metal acetate precursor by heat treatment using sol–gel process. Niasari et al. [28] developed cobalt nanoparticles from [bis (salicylidene) cobalt (II)]–oleylamine complex by thermal decomposition. Singla et al. [29] reported on the preparation and catalytic study of Ni nanoparticles stabilized by lower alkyl ammonium bromide in aqueous medium. The purpose of this study is to synthesize NiCo alloy nanoparticles with narrow size distribution in non-aqueous medium and preparation of 2D films.

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2. Experimental section

2.1. Materials

The chemicals Polyvinylpyrrolidone (PVP, M.W. 40,000) and ethanol were obtained from Loba Chemicals. Nickel chloride ($NiCl_2.6H_2O$), cobalt chloride ($CoCl_2 \cdot 6H_2O$) and acetone were acquired from Spectrochem; hydrazine hydrate ($N_2H_4 \cdot H_2O$) was supplied by Qualigen. Sodium hydroxide (NaOH) used was from S.D. Fine – Chemicals limited. Stearic acid was obtained from Sigma-Aldrich with a quoted purity of >99%. It was used without further purification. Chloroform and methanol for washing and dispersing nanoparticles were obtained from Loba Chemicals. During the whole experiment de-ionized water from Elga pure lab equipment (resistivity ~18.2 MΩ cm) was used in trough of LB System. Indium titanium oxide coated glass slides and quartz slides were chosen as a substrate for LB film deposition.

2.2. Physical measurements

The X-ray diffraction (XRD) patterns were recorded in a Rigaku D max III C Diffractometer using Cu Kα radiation, with 40 kV and 40 mA, at 0.050° scan rate (in 2θ) with a step of 3 s per point. Transmission electron microscope (TEM) measurements were done using JEOL-1200EX instrument operated at 120 kV instrument. The samples for observation were prepared by evaporation of one drop of chloroform–methanol dispersion of nanoparticles on to carbon films supported on standard holey copper grid. Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA) was done on dry powder sample using SDT Q 600 TA instrument. The powder sample was heated at the rate of 10 °C min^{-1} in the presence of inert atmosphere. For centrifuge SIGMA Laboratory Centrifuge 3K3O at the speed of 20,000 rpm was used. The ratio of Ni and Co was determined by Energy-dispersive X-ray spectroscopy (EDS) analysis machine (QUANTA, Fri Company). A commercially available Teflon Langmuir–Blodgett film deposition instrument (Apex Instruments Co.) was used for growth of monolayer/multilayer film. Atomic force microscope (AFM) measurements were performed using a Veeco Explorer instrument (USA) in non-contacting mode with the tip of Antimony doped Silicon (thickness: 2.5–3.5 μm, length: 20–200 μm, width: 23–33 μm, resonance frequency: 60–100 kHz, coating of cobalt–chromium on both sides of 1–10 nm). UV–Visible spectrophotometer of Perkin Elmer lambda 35 with 1 cm quartz cuvette was used for absorption measurements of solid film (Quartz substrate). The weighing balance used to weigh the nanoparticles was METTLER TOLEDU AX 250 Max. 220 g with an accuracy ±0.01 mg.

2.3. Synthesis of nickel–cobalt alloy nanoparticles in ethanol

An appropriate amount of 3.3 mM $NiCl_2 \cdot 6H_2O$ and 0.42 mM $CoCl_2 \cdot 6H_2O$ in the ratio of 8:1 were mixed in 60 mL ethanol at room temperature. A 0.025 g of PVP was added in this solution and the mixture was stirred until the total dissolution of the PVP, then 8 mL of hydrazine hydrate followed by 1.7 mL of NaOH (from1M NaOH solution) was added under strong magnetic stirring. After this, solution was heated up to 60 °C with constant shaking and within 5 min the solution turns black indicating the synthesis of NiCo alloy nanoparticles. During synthesis, no additional nitrogen atmosphere was used, as hydrazine itself release N_2 gas on its decomposition. The acetone was added in excess in order to precipitate out the nanoparticles. This colloidal solution was cooled in ambient conditions at room temperature. The resulting solution was ultra-centrifuged at 20,000 rpm at 15 °C, and particles were collected and washed several times with chloroform methanol mixture (1:1). After washing the nanoparticles were dried in vacuum and stored for further studies. The flowchart representing the whole process is summarized in Fig. 1.

2.4. Deposition of LB films

1 mg NiCo alloy nanoparticles were dispersed in 10 mL chloroform containing 10 mg stearic acid (typically 0.1 mg mL^{-1}). 0.9 mL of the above solution was spread dropwise on the water surface of a LB trough using a Hamilton microsyringe. The nanoparticle surface layer was monitored with a Wilhelmy plate. The LB film deposition system was controlled by WinLB computer software. Isotherm compression and data collection were automatically executed through the use of computer software. The nanoparticles were compressed by moving the barriers at a speed of 1 mm min^{-1}. The surface pressure isotherm was recorded throughout the compression process. At different stages of compression, the nanoparticles at the water–air interface were transferred carefully by retracting a hydrophilic glass substrate, which was immersed vertically in the pure water in the trough before the particle suspension was spread. The retracting speed was controlled at 1 mm min^{-1}. All the nanoparticles films described below were prepared at a constant surface pressure of 30 mN m^{-1} unless specified otherwise. Under similar condition a LB film of pure stearic acid was also grown on a glass substrate.

3. Results and discussion

3.1. Structural characterization of NiCo alloy nanoparticles

The XRD pattern of the NiCo alloy nanoparticle is shown in Fig. 2. The particle size was calculated from three major peaks using the Scherrer formula [24]

$$D = 0.9\lambda / \beta \cos\theta$$

Where β is the full width half maximum (rad), λ the wavelength Cu Kα (1.5444 Å) of the X-ray, θ the angle between the incident and diffracted beam (degree) and D the crystallite size of the sample (nm).

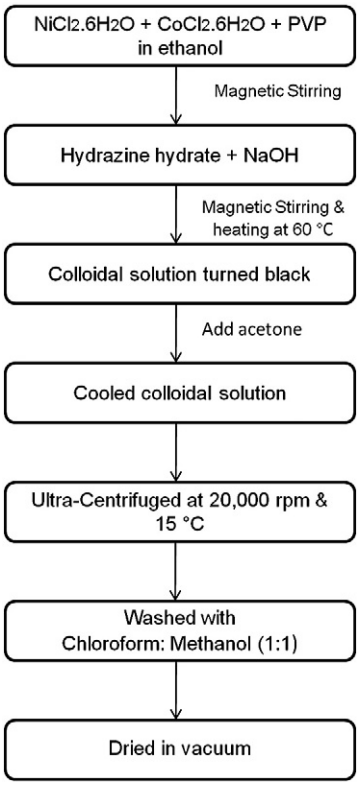

Fig. 1. Schematic representation of the synthesis procedure of NiCo alloy nanoparticles.