# Cobalt Nanoparticles: synthesis and Langmuir−Blodgett Monolayer Formation

I.N. Repina, M.E. Sokolov

Kuban State University, Krasnodar, Russia, arhiiren@inbox.ru

## ABSTRACT

In this paper, we report the synthesis of monodisperse Co nanoparticles with different sizes and formed the 2D arrays structures of the Co nanoparticles. The Co nanoparticles were chemically synthesized through a redox method in spherical micelles of the microemulsion $C_{17}H_{35}COONa$. The structure of the nanoparticles cold be clearly observed by the transmission electron microscopy (TEM) depending on the ratio of the $C_{17}H_{35}COONa$ / $Co^{2+}$. Two-dimensional arrays of the Co nanocrystals were assembled by using the Langmuir−Blodgett (LB) method. The particles were evenly distributed on the entire substrate, and their surface coverage and density can be precisely controlled. The optical properties of the microemulsions were investigated using UV-vis absorption spectroscopy. The morphology properties of the LB films were investigated using atomic force microscopy (AFM).

***Keywords***: Co nanocrystals, micellar solution, monolayers, Langmuir-Blodgett (LB) films, UV-vis absorption spectroscopy.

## EXPERIMENTAL SECTION MATERIALS

The anionic surfactant $C_{17}H_{35}COONa$ was obtained from Sigma. Cobalt chloride and sodium borohydride were supplied by Sigma. All the reagents were of analytical degree and used without further purification. The deionized water and absolute alcohol was degassed by bubbling argon through the water for 6 h.

## SYNTHESIS OF Co NANOPARTICLES

The Co nanoparticles were chemically prepared through a redox method in spherical micelles of the microemulsion $C_{17}H_{35}COONa$. The reaction was carried out under argon protection at room temperature, stirred at a given speed and ultrasonic force.

The Co nanoparticles were prepared by the reduction of $Co^{2+}$ with $NaBH_4$. A micellar solution of 0.0001M C17H35COONa and 0.001M (0.005M; 0.01M; 0.02M; 0.05M) CoCl2 (we used series of the solutions $CoCl_2$ with different concentrations of $Co^{2+}$: 0.001M; 0.005M; 0.01M; 0.02M; 0.05M) is mixed with 0.0001M $C_{17}H_{35}COONa$ micelles containing $NaBH_4$, as reducing agent. Immediately after mixing, the micellar solution remains optically clear and its color turns from yellow to black, indicated the formation of colloidal particles. The solution was centrifuged at 3000 rpm for 5 min. The precipitate was washed twice with the degassed, absolute ethanol. Finally, the precipitate was dispersed in 3 mL of ethanol.

For mechanism studies, several aliquots of the reaction mixture were collected in an appropriate time during the reaction, and checked by UV−Vis spectroscopy.

## LANGMUIR−BLODGETT LAYER FORMATION

LB experiments were done with deionized water on a LB trough (KSV IMINITROUGH 2, Finland) at room temperature. The surface pressure was monitored with a Wilhelmy plate, and was adjusted to zero before spreading the particles. The Co nanoparticles was dissolved in ethanol. This solution of was slowly spread on the water surface of the trough. The resulting surface layer was compressed by moving the mobile barriers.

## CHARACTERIZATION

Transmission electron microscopy (TEM) experiments were made on a JEOL JSPM microscope operated at 5 and 10 kV. Imaging was performed using a JEOL JSPM – 5400 atomic force microscope (AFM) under ambient conditions using a 2 $\mu$m × 2 $\mu$m scanner and a NSC35/AlBS contilever (MikroMasch) in semicontact mode. Images were obtained from at least five macroscopically – separated areas on each sample. Representative images are presented below. UV−Vis absorption spectroscopy experiments were carried out on a Hitashi U-2900 UV-vis spectrophotometer. Fonts and Spacing

## RESULTS AND DISCUSSION

2D - ordered magnetic nanoparticles are of great interest for many potential applications such as optical [1, 2] and electronic [3-5] devices, data storage devices and high-sensitivity sensors [6, 7]. Two-dimensional ordering can be achieved by the Langmuir - Blodgett (LB) technique [8] which can be combined with synthesis of nanoparticles in the microemulsion.

Often nanoparticles synthesized in reverse micelles. It is not always convenient. In this work, we report the synthesis of Co nanoparticles in spherical micelles and formations the 2D arrays structures of Co nanoparticles.

The cobalt (Co) nanoparticle is one of the most promising nanomaterials for electronic and information

storage devices because it has one of the largest magnetic susceptibilities as compared to other metal nanoparticles.

## 1. CMC

It is known that in solution, amphiphilic molecule (a surfactant) self assemble to form aggregates. This kind of organization of surfactant molecules can be described as a micelles. In general, spherical micelles form to achieve the lowest interfacial area. The typical diameters of spherical micelles are around 3 – 6 nm. So, we have a chance to control of the shape and diameter nanoparticles which can be obtained in the micelles.

The particle size is controlled by the critical micelle concentration (CMC) of the surfactant. The critical micelle concentration (CMC) was determined by the measurement of the electrical conductance of the micellar solution $C_{17}H_{35}COONa$. The CMC for $C_{17}H_{35}COONa$ = 0.0001M.

## 2. UV−Vis

The reaction progress of Co nanoparticles synthesis was monitored by UV−Vis absorption to support this mechanism. The color of the solution immediately changed from yellow to dark, indicating the fast reduction of $Co^{2+}$ to $Co^0$ species (Fig. 1).

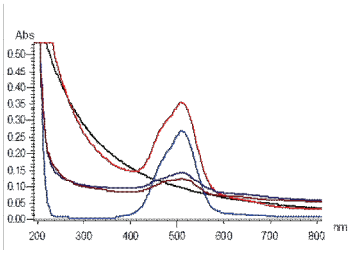


**Fig.1**. UV−Vis absorption spectra of the Co sample during the reaction. A micellar solution of 0.0001M $C_{17}H_{35}COONa$ (black); 0.01M $CoCl_2$ (blue);the aliquots were collected 0 (red), 10 (dark blue), 30 (dark red) min after the addition of $NaBH_4$.

## 3. SEM

The structure and size distribution of the Co nanoparticles is confirmed by the TEM, as shown in Fig. 2.

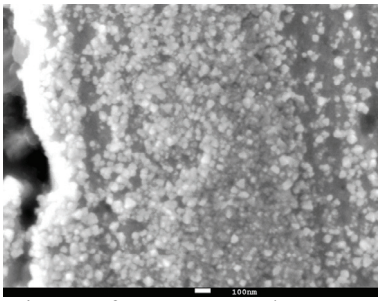


**Fig.2.** SEM image of Co nanocrystals.

TEM images show the presence of nonagglomerated and moderately monodispersed spherically shaped Co nanoparticles with a different diameter depending on the ratio of the $C_{17}H_{35}COONa$ / $Co^{2+}$ in the micellar solution and ranges from 20 to 100 nm.

## 4. LANGMUIR−BLODGETT LAYER FORMATION OF Co NANOPARTICLES

Two-dimensional arrays of the Co nanoparticles were assembled by using the LB method. The particles were evenly distributed on the entire substrate, and their surface coverage. The surface morphology of 1 layer LB films of Co nanoparticles is shown in Fig. 3.

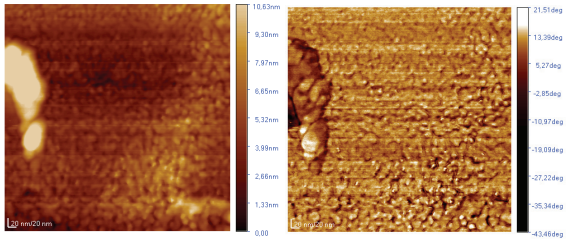


**Fig 3.** Height and phase AFM images (500 nm x 500 nm) of Co nanoparticles on mica.

We observed that the size of the resulting particles is of the order of 10-15 nm. The resulting Co LB layers are potential candidates for 2-D model data storage devices as a result of their high structural uniformity of the metal nanoparticles.

[1] Yoffe, A. D. Semiconductor Quantum Dots and Related Systems: Electronic, Optical, Luminescence and Related Properties of Low Dimensional Systems. Adv. Physics 2001, 50, 1–208.

[2] Kamat, P. V. Photophysical, Photochemical and Photocatalytic Aspects of Metal Nanoparticles. J. Phys. Chem. B 2002, 106, 7729–7744.

[3] Feldheim, D. L.; Keating, C. D. Self-Assembly of Single Electron Transistors and Related Devices. Chem. Soc. Rev. 1998, 27, 1–12.

[4] Park, J. I.; Kang, N. J.; Jun, Y. W.; Oh, S. J.; Ri, H.C.; Cheon, J. Superlattice and Magnetism Directed by the Size and Shape of Nanocrystals. ChemPhysChem 2002, 3, 543–547.

[5] Schmid, G. Nanoclusters—Building Blocks for Future Nanoelectronic Devices. Adv. Eng. Mater. 2001, 3, 737–743.

[6] Vossmeyer, T.; Guse, B.; Besnard, I.; Bauer, R. E.; Mullen, K.; Yasuda, A. Gold Nanoparticle/Polyphenylene Dendrimer Composite Films: Preparation and Vapor- Sensing Properties. Adv. Mater. 2002, 14, 238–242.

[7] Krasteva, N.; Fogel, Y.; Bauer, R. E.; Mullen, K.; Joseph, Y.; Matsuzawa, N.; Yasuda, A.; Vossmeyer, T.

Vapor Sorption and Electrical Response of Au-Nanoparticle-Dendrimer Composites. Adv. Funct. Mater. 2007, 17, 881–888.

[8] Coronado, E.; Mingotaud, C. Hybrid organic/inorganic Langmuir-Blodgett films. A supramolecular approach to ultrathin magnetic films. Adv. Mater. 1999, 11, 869-872.